STUDIES OF HYDROGENATION AND HYDRODESULPHURISATION REACTIONS CATALYSED BY MOLYBDENUM DISULPHIDE

THESIS

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ABSTRACT

The interaction of buta-1:3-diene and thiophen with hydrogen has been investigated over molybdenum disulphide catalysts. The adsorption of hydrogen sulphide over these catalysts has also been studied, using a [^{35}S] radiotracer technique, and the effect of adsorbed 'sulphur' upon the buta-1:3-diene hydrogenation reaction investigated.

The results of the investigation of the hydrogenation of buta-1:3-diene over freshly prepared, used and sulphided catalysts show that two types of catalyst surface can be characterised in terms of the distribution of the n-butenes formed in the hydrogenation of buta-1:3-diene. The type 'A' surface, characteristic of a freshly prepared catalyst which had been subjected to a number of buta-1:3-diene hydrogenation reactions, produced a high initial yield of but-1-ene and a trans-:cis-but-2-ene ratio of approximately 1.5. The type 'B' surface, characteristic of a type 'A' catalyst which had been sulphided, either by carrying out a series of thiophen hydrodesulphurisation reactions or by treating the catalyst with hydrogen sulphide, gave a relatively low initial yield of but-1-ene, with trans-but-2-ene as the major product. The type 'A' and 'B' surfaces exhibited very similar activities for the buta-1:3-diene hydrogenation.

Studies of the adsorption of hydrogen sulphide and of the exchangeability of the catalyst sulphur, using a [^{35}S]

radiotracer method, showed that, whilst the amount of hydrogen sulphide required to convert a type 'A' catalyst surface to a type 'B' surface was $\sim 5 \times 10^{18}$ molecules per gramme of catalyst, further hydrogen sulphide uptake, up to 8.68×10^{19} molecules per gramme of catalyst, could be observed. Only a limited amount of hydrogen was produced from the interaction of the hydrogen sulphide with the catalyst surface, the ratio ($H_2S_{ads}/H_{2formed}$) having a value of approximately four. The type 'B' surface was capable of undergoing sulphur exchange with [^{35}S]-hydrogen sulphide to an extent approximately equal to the amount of sulphur required to bring about the transitions from a type 'A' to type 'B' surface. No sulphur exchange was possible with the type 'A' catalyst, although a limited (ca 1%) amount of sulphur exchange was observed with a freshly prepared sample of molybdenum disulphide.

Both the type 'A' and type 'B' catalysts showed reproducible behaviour in buta-1:3-diene hydrogenation. There was no tendency for either surface to convert from one type to the other as a consequence of its usage for buta-1:3-diene hydrogenation. However, whilst the type 'A' surface could be readily converted to a type 'B' surface by sulphidation at 350°C, the type 'B' to type 'A' conversion was more difficult, requiring stringent conditions of treatment in nitrogen at 750°C, or in oxygen at 350°C.

The observations made during these studies are interpreted

in terms of a mechanism whereby the hydrogenation of buta-1:3-diene occurs at coordinatively unsaturated surface molybdenum ions either by a predominantly 1:2-hydrogen addition (type 'A') or a 1:4-hydrogen addition (type 'B') process. The adsorption of hydrogen sulphide, either directly or as a result of thiophen hydrodesulphurisation, is interpreted in terms of the formation of surface hydrosulphide ions, together with some incorporation of sulphur in the molybdenum disulphide lattice, and, in consequence, the major difference between the types 'A' and 'B' surfaces is considered to be found in the different degrees of coordinative unsaturation of the active surface molybdenum ions. This may result in the two types of surfaces having active surface molybdenum ions in differing oxidation states; the type 'B' surface being oxidised relative to the type 'A' surface, or, alternatively, may result in changes in the availability of hydrogen for the 1:2- and 1:4-addition processes at the two types of surface, the latter process being favoured at the lower degree of coordinative unsaturation proposed with the type 'B' surface.

CONTENTS

CHAPTER 1

1. INTRODUCTION

1.1 General introduction

Fundamental research into the field of catalysis using sulphide catalysts has been widely developed since 1930 when sulphide catalysts were developed for use in coal and tar processing. The sulphide catalysts began to be used in petroleum processing in the late 1940's especially in hydro-treating and hydrorefining of petroleum products.

Sulphide catalysts are now used where the raw materials contain substances which are catalytic poisons to metal catalysts. Conventional poisons, usually of sulphur containing compounds (mercaptans, sulphides, heterocyclic sulphides etc.), are catalysed by metal sulphides or by catalysts in which the sulphide component plays a decisive catalytic role. The catalysts may be used either in the pure form or supported on a carrier; individual sulphides may be used or mixtures of metal sulphides in different combinations and ratios. The activity and lifetime of the catalyst is enhanced by adding promotors. The catalysts used in hydrode-sulphurisation of various sulphur containing compounds are usually formed from alumina-supported oxides of cobalt and molybdenum and the surfaces are usually sulphided in operation. Catalysts of this type are often referred to as cobalt molybdate. Industrial catalysts may contain as much as 10 to

20 percent of cobalt and molybdenum. A number of other mixed sulphides have also been used for example, nickel and tungsten istead of cobalt and molybdenum for hydrodesulphurisation. The sulphides of the group VI metals are also good hydrogenation catalysts with the added advantage of stability in the presence of organo sulphur compounds and hydrogen sulphide.

When compared with other catalysts, sulphide catalysts have a special position due to their outstanding resistance to the effect of poisons. Conventional poisons, especially sulphur compounds, not only do not diminish the catalytic activity, their presence in fact maintain a high activity and long lifetime of the catalyst. Sulphide catalysts are also quite resistant to the formation of carbonaceous materials on the surface of the catalyst.

1.2 Physico-chemical properties of sulphide catalysts

1.2.1 The crystal structure of the sulphide catalysts

The two most important catalytically active sulphides, MoS_2 and WS_2 have a similar crystal structure. Both occur in two crystallographic modifications (1) namely hexagonal and rhombohedral.

The structure of molybdenite is shown in figure 1.1 (2). In the hexagonal molybdenite lattice the individual crystallite layers are oriented antiparallel around the c-axis

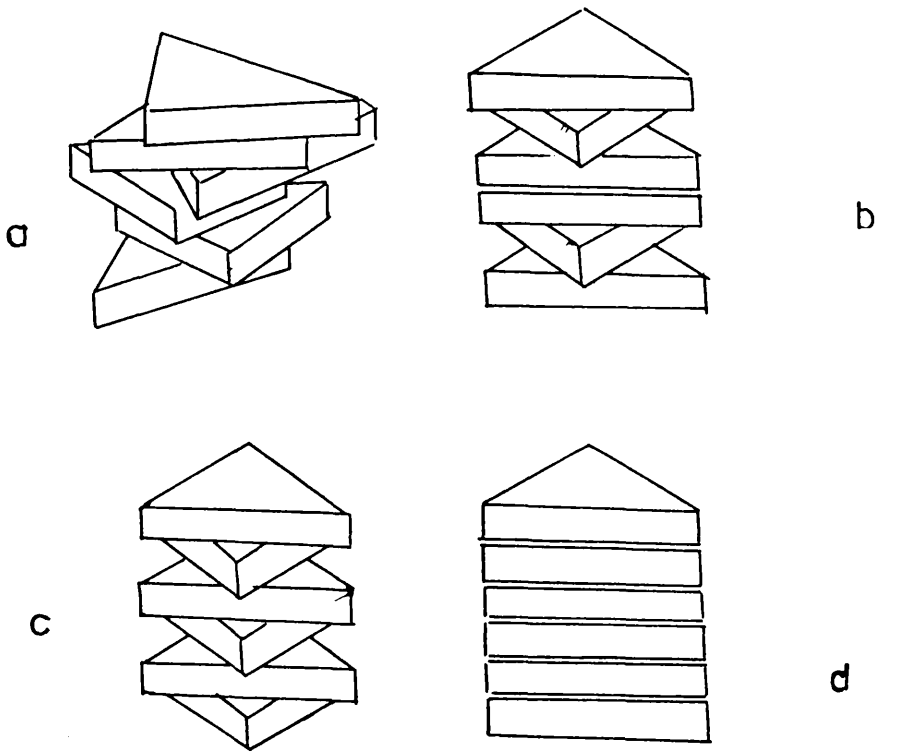


Figure 1.1 Structure of MoS_2: random stacking of individual layers (a). Hexagonal MoS_2 with stacking faults (b). Hexagonal MoS_2-neighbouring crystallite layers are oriented antiparallel (c). Rhombohedral MoS_2-parallel orientation of crystallites around the C-axis (d).

(figure 1c) and the metal layer is separated by two layers of sulphur atoms. The structure of the rhombohedral modification is shown in figure 1.1d. A high yield of this modification is obtained by alkaline fusion of MoO_3 (1) with sulphur. This modification is unstable and on heating converts into hexagonal MoS_2 (1). Other structures may be present due to more or less extensive randomisation of the orientation of the layers around the c-axis. This defective structure is accompanied by the presence of excess of sulphur and the existence of molybdenum vacancies. These structures are shown in figure 1.1a and 1.1b (2).

Thermal decomposition of MoS_3 has been studied by means of thermal analysis and by an X-ray study carried out by Widervanck and Jellinck (1). Dissociation of MoS_3 and the formation of the hexagonal MoS_2 modification on heating to different temperatures in the range of 400 to 1000°C may be illustrated as shown in figure 1.2. On heating to 350°C, MoS_3 loses some sulphur, while the product continues to be amorphous. The non-arranged crystallite aggregates begin to form at 350 to 400°C (a). Further heating to 500°C results in aggregation around the c-axis, whilst the crystallite arrangement continues to be random. At this stage the anti-parallel orientation of the crystallite begins to develop (b). At 800°C the hexagonal structure is formed but it still has a considerable number of defects (c). At 1000 to 1100°C the hexagonal structure is complete. Wildervanck and Jellinck (1)

did not observe any formation of the rhombohedral modification in their studies.

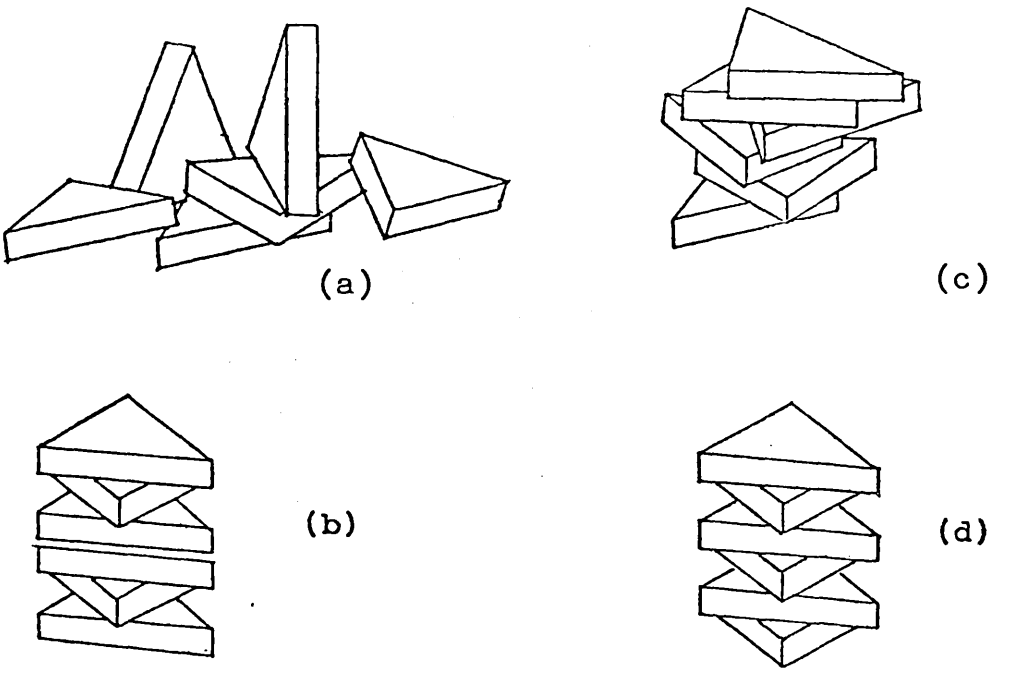


Figure 1.2 The models of the gradual build-up of the hexagonal MoS_2 lattice (a,b,c,d).

Sulphides of nickel are important in preparing active catalysts. They are usually NiS and Ni_3S_2. NiS exists in three modifications: α-NiS is amorphous, β-NiS is trigonal and γ-NiS forms the hexagonal structure (3). An equilibrium is established between β- and γ-modification at medium temperature; the hexagonal modification is stable above 396°C, whilst the trigonal form is stable below this temperature. At higher temperature in a reducing atmosphere, however, NiS transforms to NiS_2. The subsulphide Ni_3S_2 is dimorphous.

Cobalt is an active component of cobalt-molybdate refining

catalyst, which converts in part to the sulphide form on sulphidation. In the literature five cobalt sulphides have been identified, namely Co_4S_3, CoS, Co_3S_4, Co_9S_8 and CoS_2 (4). Richardson (5) explains that under desulphurisation conditions, Co_9S_8 (which itself is of low catalytic activity) is present in the active catalyst, whilst the remaining cobalt is bound partly in a nonactive spinal $CoAlO_4$ and in part as the highly active complex Co-MoS_2.

1.2.2 Texture and adsorption characteristics of sulphide catalysts

Investigation of textural properties of sulphide catalysts has been receiving increased attention in recent years. Most of the textural data is concerned with the industrially important sulphides of tungsten, molybdenum and nickel. Among these catalysts WS_2 is widely used in industry and has attracted more attention than the other sulphides. The adsorption and other surface properties are complicated by the difficulty of obtaining an absolutely pure sulphide surface, free of non-stoichiometric sulphur, sorbed gases, sulphuric acid etc.

Donath (6) has characterised WS_2 by a high degree of selectivity for hydrogen and olefins adsorption. The pre-treatment of WS_2 catalyst influences the amount of hydrogen that is adsorbed. From studies of hydrogen adsorption on a catalyst which was degassed for several hours at 300^{o}C and

another catalyst which had been pretreated with hydrogen at 300°C for several hours and then degassed, Donath (6) concluded that hydrogen pretreatment of the catalyst increased the amount of hydrogen adsorbed. The adsorption capacity of deactivated WS_2 (the deactivation being brought about by prolonged use), was compared to that of the fresh catalyst. The adsorption capacity of the deactivated catalyst was considerably lower.

Several studies have been carried out of the adsorption of benzene and n-heptane (7,8), the rare gases, argon and krypton (9,10) and high molecular weight n-paraffin (11) on MoS_2. Adsorption of hydrogen, furan, tetrahydrofuran, thiophene and tetrahydrothiophene have been studied (12,13) on MoS_2 and $MoS_2.MoO_2$. The surface area of both of the catalysts was $\sim 17\ m^2\ g^{-1}$. Activated adsorption started on each catalyst at 150°C. The extent of the adsorption of thiophene over $MoS_2.MoO_2$ was about five times that of hydrogen adsorption.

There are several reports concerning hydrogen sorption by sulphide catalysts (6,14). Wright et al. (14) measured the amount of hydrogen sorbed by MoS_2, using the inelastic neutron scattering technique. They demonstrated that the hydrogen uptake was several times greater than would be expected on the basis of the nitrogen surface area. The results revealed that hydrogen either entered the lattice of MoS_2 or it was sorbed in sites (dislocations) that are inaccessible to nitrogen

molecules. It was concluded that hydrogen reacts with supported catalyst to form H-S groups in MoS_2 crystallites. However there was no evidence for the presence of SH_2 groups or molecular hydrogen on the surface of MoS_2. Massoth (15) had made a quantitative estimation of hydrogen absorbed by supported MoS_2 catalysts, when alumina-supported molybdenum oxide was sulphided and reduced at 400°C. It was shown that the atomic ratio of hydrogen sorbed to molybdenum was 1.26:1; which was interpreted in terms of a surface covered with a large number of $Mo\begin{matrix}S\text{-}H\\S\text{-}H\end{matrix}$ groups. However there was no spectroscopic evidence for this model. Although Wright et al. (14) successfully derived some information about the equilibrium structure of hydrogen sorbed by MoS_2, the mechanism of this process still remains obscure.

Lukens et al. (16) have described an advantageous method of measuring the specific surface areas of supported metal sulphides using [^{35}S]-hydrogen sulphide. As the surfaces of the sulphide are very non-stoichiometric, under sulphiding conditions, the surface may contain excess sulphur, whilst under reducing conditions it may be deficient in sulphur. In the presence of oxygen or air, the surface sulphide atoms can be replaced by oxygen atoms. For this reason the catalysts were subjected to various pretreatments. The samples were evacuated (1 - 4 hours) at 275°C followed by treatment with a mixture of hydrogen and hydrogen sulphide (10:1) at 275°C. The exchange values were somewhat different from the values expected from a theoretical consideration of the crystal

unit cell. The discrepancy was thought to be due to the non-stoichiometric surface of the catalyst. In the same experiment, Lukens (16) determined the specific surface areas of three supported metal sulphides using the radiotracer technique. Although these catalysts varied widely in their total surface areas and in the amounts of sulphide present, they exhibited approximately equal activities for the hydrogenation of α-methylnapthalene. Examination of the sulphide catalysts by the [^{35}S]exchange technique revealed that all had comparable sulphide areas per gram of catalyst.

The isotopic exchange technique was neither precise nor rapid as compared to the BET method for measuring total surface area, yet it provided information which was not attainable by other methods.

The surface area of MoS_2 formed by the decomposition of MoS_3 in a hydrogen or inert atmosphere depends upon the rate of heating to the temperature of decomposition of MoS_3 to MoS_2 (17). When MoS_3 was heated rapidly to 450°C, the MoS_2 catalyst so formed had a considerably higher surface area up to 158 m^2/g as compared to that of the MoS_2 catalyst (2 m^2/g) obtained by heating slowly to 450°C.

Wilson et al. (18) have carried out studies of the exchange reactions between hydrogen sulphide and deuterium and between hydrogen and deuterium over MoS_2 and WS_2. The exchange reactions over both the catalysts were somewhat similar. It was concluded that over both catalysts the

hydrogen + deuterium exchange reaction was a more rapid reaction than the hydrogen sulphide + deuterium exchange reaction and that hydrogen sulphide was adsorbed more strongly than hydrogen on MoS_2. Donath (6) showed that the adsorption of hydrogen takes place rapidly on WS_2 at $0^{o}C$. However some reversible chemisorption must occur at lower temperatures because there was an appreciable rate of exchange between hydrogen and deuterium at $-78^{o}C$ (18). The production of gas phase hydrogen as the result of hydrogen sulphide and deuterium exchange reaction was explained by two possible schemes viz.

Scheme I

$$H_2S(g) \longrightarrow S(a) + H_2(g)$$

$$D_2(g) + S(a) \longrightarrow D_2S(g)$$

Scheme II

$$H_2S(g) \longrightarrow HS(a) + H(a)$$

$$D(a) + HS(a) \longrightarrow HDS(g)$$

The reaction kinetics observed for the hydrogen sulphide + deuterium reaction, approximately first order in deuterium and zero order with respect to hydrogen sulphide, were consistent with Scheme I, as hydrogen sulphide is known to be strongly adsorbed. Scheme II was applied by considering certain conditions (i) the deuterium is weakly adsorbed on sites which were not occupied by sulphur atoms (ii) there is strong adsorption of the species S(a) and SH(a) so that the total concentration of these two species is independent of

the pressure of hydrogen sulphide (iii) the amount of HS(a) is small as compared with S(a). There was evidence for the formation of some hydrogen deuterium sulphide on MoS_2 at 140 to 200°C during the exchange reactions between hydrogen and deuterium, which was probably due to the fact that the surface of MoS_2 is not stable and could be reduced in this range of temperature.

Infrared spectroscopic techniques have been widely used to characterise different states of Co-Mo/Al_2O_3 type catalysts (19-23). Infrared spectroscopy of adsorbed hydrogen sulphide over unsupported MoS_2 however failed to give much information about the mode of adsorption (24). Infrared spectroscopic studies of hydrogen sulphide adsorption on alumina-supported MoS_2 and on alumina alone were carried out by Slager and Amberg (25). In these studies major infrared bands at 1341, 1568, 1625 and a broad band centred around 3400 cm^{-1} over alumina were observed. On alumina-supported MoS_2, two significant bands appeared, which were similar to those observed on the support alone. The band frequencies were, however, lower by about 5 to 10 cm^{-1} than those observed on alumina and closer to those for the adsorbate in the gaseous state. This was taken as evidence that the hydrogen sulphide molecule was less perturbed by adsorption on the MoS_2/Al_2O_3 catalyst than on Al_2O_3, probably due to the significant decrease in the concentration of oxygen atoms exposed on the surface. Hydrogen bonding is known to be much weaker

to a sulphur atom than to an oxygen atom. Consequently hydrogen did not interfere with the adsorption of hydrogen sulphide on a sulphide surface. Tropsøe (26) has carried in situ infrared studies of Co/Al_2O_3, $Co\text{-}Mo/Al_2O_3$, $MoS_2 + Al_2O_3$ (physical mixture) and the Al_2O_3 support itself, to investigate the surface structure of sulphide catalysts. Infrared spectra of these catalysts both in their oxidic and sulphidic states were obtained and the following conclusions were made.

(a) There was a close similarity of the spectra for Co/Al_2O_3 and Al_2O_3 alone in their oxidic (non-sulphidic) state. The addition of molybdenum to alumina (3% Mo/Al_2O_3), however showed the disappearance of bands ascribable to surface hydroxyl groups. From the spectral evidence it was postulated that cobalt might have interacted with molybdenum in $Co\text{-}Mo/Al_2O_3$ catalyst in their oxidic state.

(b) On sulphiding the catalysts, the spectra of Al_2O_3 and Co/Al_2O_3 was unchanged and as found in their oxidic states thereby verifying that the cobalt ion did not interfere with the hydroxyl group of alumina. Sulphided Mo/Al_2O_3 catalyst showed a very broad band centered around 3580 cm^{-1} showing that there was an extensive hydrogen bonding on the surface of the catalyst. The sulphided $Co\text{-}Mo/Al_2O_3$ showed a broad band (broadening was less than in the case of Mo/Al_2O_3) centered around 3600 cm^{-1} which revealed that the association of Co with Mo/Al_2O_3 could be attributed to a decrease in the extent of hydrogen bonding.

(c) The spectra of a physical mixture of MoS_2 + Al_2O_3 was found to be similar to that of the sulphided Al_2O_3.
(d) Contrary to the findings of Slager (25) there was no evidence of the presence of SH species in the spectra of sulphided catalysts. Rather the data suggested that a strong interaction of molybdenum with the alumina surfaces occurred both in their oxidic and sulphidic forms.

Mitchell and Trifiro (21) reported that the sulphided Co-Mo/Al_2O_3 catalyst did not resemble any known sulphides of cobalt or molybdenum. They proposed a surface O - Mo^{6+}- S species to be present. These conclusions were supported by X-ray photoelectron (ESCA) spectra of the sulphided catalysts, which showed the presence of Mo^{6+} and a small amount of reduced molybdenum species (27). However the results of Mitchell and Trifiro (21) must be considered inconclusive, since their sulphided sample was apparently exposed to air before running the infrared spectrum. Progressive reoxidation of the sulphided catalysts by heating in air restored the infrared spectrum of the fresh catalyst.

The chemisorption of hydrogen over unsupported MoS_2 was studied and the mode of SH stretching was monitored by using infrared spectroscopy (24). These studies provided valuable information about the chemisorption of hydrogen over unsupported MoS_2. Two samples of catalysts namely MoS_2I (BDH commercial catalyst), MoS_2II (a laboratory prepared catalyst from MoS_3). Both catalysts exhibited two distinct

absorption bands in the region of 2500 - 2700 cm^{-1}; a characteristic of the SH stretching vibration. MoS_2(I) exhibited absorption bands at 2640 and 2500 cm^{-1} and similar features were observed in the spectrum of MoS_2(II). Interesting results were obtained when hydrogen was adsorbed on MoS_3; at 25°C a broad spectrum centered around 2500 cm^{-1} was observed, upon heating at 100°C and 200°C the bands shifted to 2525 and 2516 cm^{-1} respectively. When the sample was evacuated at 300°C, three distinct bands centered at 2454, 2532, and 2649 cm^{-1} appeared and persisted, though with a diminished intensity, even after evacuation at 400°C. The presence of two bands in MoS_2 were interpreted as showing the presence of two different lattice sites in the catalyst or, alternatively, the presence of hydrogen bonds of different strength which can be explained as being due to the weakness of the S - H ... S bonds arising from the more covalent character of the S - H linkage. On MoS_2, SH bonds may be linked at either Mo^{4+}, Mo^{3+} or Mo^{2+} cations, the former will give rise to the band at 2490 $\pm$ 10 cm^{-1} and the latter to the 2635 cm^{-1} band. The most probable presence of anion vacancies neighbouring to SH group could also increase the SH stretching frequency, since the electrical field acting on SH is a result of the distribution of the cationic and anionic charges in the environment.

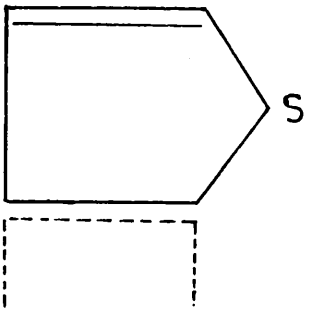
Infrared spectroscopic methods have been used to study the adsorbed state of thiophene on unsupported MoS_2 and on

sulphided Co-MO/Al_2O_3 by Nicholson (28,29), on unsupported MoS_2 and on Co-Mo/Al_2O_3 (23,24). Ratnasamy and Fripiat (24) carried out detailed studies of thiophene adsorption studies using an unsupported MoS_2 catalyst which was reduced in hydrogen at 375°C before the chemisorption of thiophene at required temperature. From the infrared studies of chemisorbed state of thiophene, they were able to observe the transformation to 1- and 2-butene and to acetylenic and vinylidenic radicals (figure 1.3).

The adsorption isotherms of thiophene on MoS_2 at various temperatures were studied (24). The activated adsorption started at 100°C. At higher temperatures the amount of thiophene adsorbed was less than at 100°C, which was probably due to the decomposition of adsorbed thiophene. The infrared results were, however, consistent with these results as the acetylenic species (D) was found to be significant at higher temperatures.

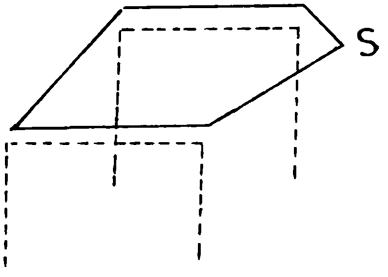
Infrared spectroscopic methods were used to study thiophene adsorption on unsupported MoS_2 and on sulphided Co-Mo/Al_2O_3 catalysts by Nicholson (28,29). Infrared spectra indicated that the surface of the sulphided Co-Mo/Al_2O_3 mainly consisted of thiophene adsorbed by a four-point attachment to the surface, whereas unsupported MoS_2 showed bands due to thiophene adsorbed in the four - as well as the two-point form. The former dominated. This was also found with MoS_2/γ-Al_2O_3, although in this case two-point adsorption

Species A



3041 cm^{-1}

or



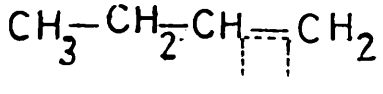
"Edge" adsorbed
(two point form)

"Flat" adsorbed
(four point form)

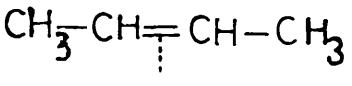
Species B

Species C

2960
2920
2850 cm^{-1}



But-1-ene



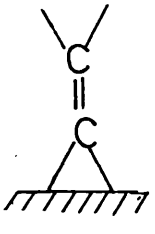
But-2-ene

3045
2960
2920
2850 cm^{-1}

Species D

3140 cm^{-1}

or



3150
3050 cm^{-1}

Acetylenic

Vinylidenic

Figure 1.3 The adsorbed states of thiophene

dominated. Addition of Co to MoS_2 resulted in the two-point adsorption form becoming the predominant species. However, under hydrodesulphurisation conditions one- and two-point adsorption was important (30). Lipsch and Schuit (31) have referred to the 'one-point' mechanism. Their data was derived largely from studies of kinetics and product distributions by Amberg and co-workers (32-36), who detected buta-1,3-diene among the products of thiophene hydrodesulphurisation.

Co-Mo/Al_2O_3 catalysts in their oxidic state are used in hydrodesulphurisation of thiophene. An infrared study of the interaction of thiophene with an oxidic form of the catalyst is, therefore of importance. The catalyst was treated with thiophene at 80°C and the infrared band of the adsorbed species was determined (23). The results showed that the oxide surface was highly reactive and decomposed the adsorbed thiophene even at low temperatures. This was further supported by the fact that infrared bands of decomposed products were present even at 80°C.

1.2.3 The electronic factor in sulphide catalysts

Although there is a significant relationship between adsorption and electrical properties of the sulphide catalysts, relatively little data is available in the literature, particularly with regard to the relationship between the defect structure of sulphide catalysts and their

hydrogenation, isomerisation and hydrodesulphurisation activity. The data available in the literature are mainly related to the electrical conductivity of molybdenum sulphide catalysts (37-42).

Systematic studies of the defect control of hydrogenation and hydrodesulphurisation activity of molybdenum sulphide and Co^{2+}-doped molybdenum sulphide catalysts were carried out by Wise and co-workers (37-39). The experimental studies were made with a single crystal of MoS_2 and the influence of foreign ions like S^{2-} and Co^{2+} was monitored by electrical conductivity and Hall coefficient measurements. The changes in the electrical properties of the catalyst crystal were monitored during both the pretreatment procedure and actual catalysis reactions.

For initial activation of the catalyst, the undoped catalyst was reduced at 627°C in the stream of hydrogen and an increase in electron density was measured. The sulphur removal from the crystal due to electron injection could be represented in either of the equations given below.

$$S^{2-} + H_2 \longrightarrow H_2S + 2e + V_a$$

or (I)

$$S^{2-} + H \longrightarrow SH^- + e + V_a$$

where e is an electron and V_a an anion vacancy.

An opposite electrical response was brought about by treatment of the catalyst in an hydrogen sulphide environment, which resulted in a decrease in electron density due to

electron capture by reaction II.

$$H_2S + 2e + Va \longrightarrow H_2 + S^{2-} \qquad (II)$$

Thus the introduction of S^{2-} anions into the MoS_2 lattice tends towards p-type conductivity, while sulphur deficiency leads to n-type behaviour. By these pretreatment procedures the defect structure of the catalyst was adjusted and its effect on catalytic activity was examined. The hydrogenation activity of the molybdenite was evaluated at 350^{o}C by injecting but-1-ene into the hydrogen carrier stream (38). A catalyst highly deficient in sulphur exhibited very low n-butane formation, whilst upon progressively sulphiding the catalyst, an increase in n-butane formation was observed. These results were in accordance with the hydrodesulphurisation of butyl mercaptan (37) in which the formation of n-butene was found to be predominant under conditions where the catalyst exhibited high conductivity. Conversely, when S^{2-} was introduced the catalyst exhibited low conductivity and the predominant product was n-butane. The extent of exposure of the catalyst to hydrogen (progressive extent of S^{2-} removal) or hydrogen sulphide (associated with a dimunition in S^{2-} ion vacancies) had a pronounced effect on catalytic activity. The electrical conductivity results indicated that the decrease in conductivity brought a marked increase in the hydrodesulphurisation activity. The gradual modification of the electronic properties of molybdenum sulphide, according to Aoshima and

Wise (37), were due to the accumulation of a charged, non-active, sulphur bearing intermediate species on the catalyst surface, most probably S^{2-} which becomes part of the crystal lattice.

When a MoS_2 catalyst doped with Co^{2+} was used for hydrodesulphurisation of butyl mercaptan and the electrical properties were monitored as a function of various pretreatments, it was found that the catalyst was (a) stable to sulphidation and reduction on exposure to a hydrogen sulphide + hydrogen mixture or hydrogen respectively, (b) catalytically more active for the production of n-butane and hydrogen sulphide and (c) relatively constant in activity with respect to both the extent of conversion and the product distribution (39). The conductivity data could be related to the defect structure of the Co-Mo sulphide by considering that the interaction at the gas-solid interface resulted in the formation of vacancies and electronic charge carriers (figure 1.4). The vacancies perturb the local potential in the solid and give rise to a localized electron energy level located between the S^{2-} band (filled valance band, E_v) and Mo^{4+} band (unfilled conduction band E_c). A localized level V_a^- will be established in the band gap, probably close to the energy level of Co^{2+} in the doped catalyst. Consequently, the electronic properties of n-type molybdenum sulphide will be affected in a similar way by adding S^{2-} anions or Co^{2+} cations to the lattice in agreement with the experimental observations.

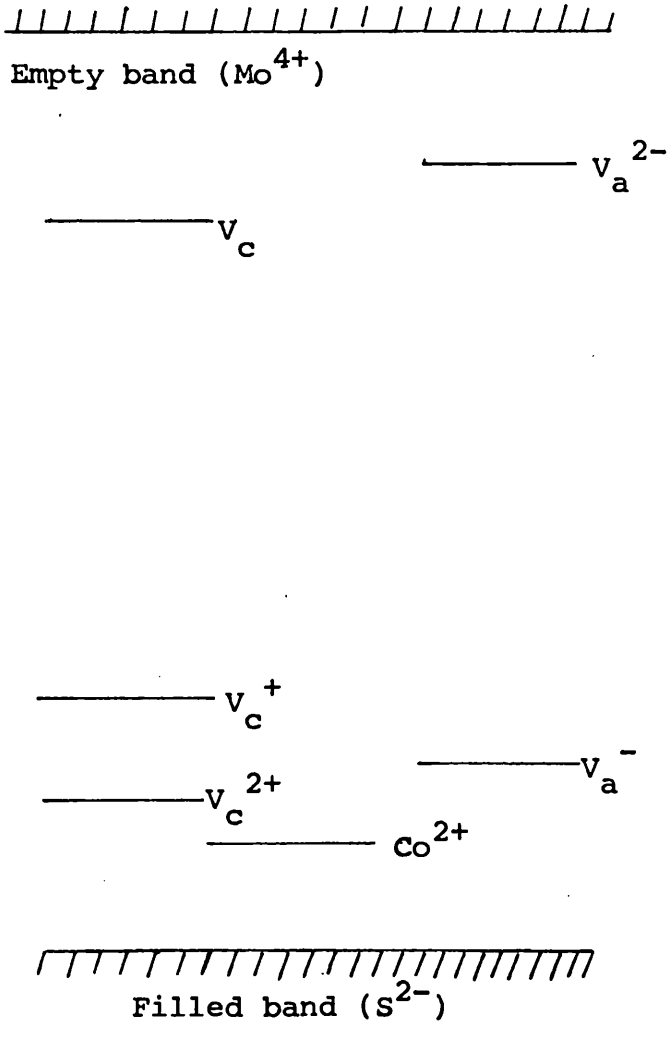


Figure 1.4 Energy diagram for Co^{2+} doped MoS_2 catalyst.

The difference could be seen between the S^{2-} rich molybdenum sulphide and the Co^{2+} doped catalyst because S^{2-} ions could be removed by the reaction of hydrogen and could cause a change in the electronic structure and its catalytic function. With the Co^{2+} doped catalyst, however, no such modifications are expected as the Fermi level is dominated by Co^{2+} cation.

1.3 The influence of non-stoichiometric sulphur

A marked change in activity of sulphide catalysts has been mentioned in section 1.2.2 in connection with the change in structure, texture and other physico-chemical properties. Analysis of these findings shows that the change in physico-chemical properties is in most cases due to changes in the sulphur content or sulphur bonding in the catalyst. The hydrogenation, isomerisation and hydrodesulphurisation activity is influenced by a decrease or increase of sulphur content; especially the non-stoichiometric sulphur of the catalyst. The effect of non-stoichiometric sulphur on the overall activity of the sulphide catalysts is reviewed in this section.

The origin of non-stoichiometric sulphur in sulphide catalysts is of significant importance. The first systematic studies concerning the behaviour of non-stoichiometric sulphur in sulphide catalysts for hydrogenation, isomerisation and cleavage activity was carried out by Kalechits and co-workers (43-45). Supporting the active catalyst MoS_2 on

an activated charcoal, with a large surface area resulted in a significant decrease in the isomerisation activity and an increase in the hydrogenation activity as compared to the values obtained with pure MoS_2 catalyst (45). An increase in the hydrogenation activity was observed with increasing dilution of the active component. The same catalyst when reduced with hydrogen also exhibited a lower isomerisation activity. Hydrogen sulphide treatment of the catalyst resulted in an increase in its isomerisation activity and such catalysts gave approximately twice as much isomerisation product as the same catalysts when reduced with hydrogen. The catalyst treated in hydrogen sulphide retained more non-stoichiometric sulphur than that reduced with hydrogen. According to these authors (45) this excess sulphur is not mechanically trapped or physically adsorbed on the surface of the catalyst but bound with stronger forces. This idea was verified by Kalechits et al. (44,45) who studied the hydrogenation reactions with benzene in the presence of carbon disulphide labelled with radioactive sulphur. The experimental results revealed that the total sulphur in the fresh catalyst may be divided into three parts. The larger part of the sulphur (90-95%) is firmly bound stoichiometric sulphur, which is not reducible and not exchangeable at all or, at least, only exchangeable with great difficulty. A small part of the catalyst sulphur is removable 'mobile'. Most of this mobile portion can be easily removed on hydrogenation

reactions. The rest of the sulphur can only be removed with great difficulty by hydrogenation reactions. This second portion, however, is exchanged for sulphur contained in the raw material containing sulphur. Both types of this non-stoichiometric sulphur (especially the firmly bound part) participate in catalytic activity. The isomerisation and cleaving activity decreased with gradual removal of non-stoichiometric sulphur and increased sharply with addition of carbon disulphide. The authors (44,45) believed that the more strongly held non-stoichiometric sulphur behaved as an acceptor impurity; reducing the Fermi level and increasing the positively charged particles on the catalyst surface. When the reaction is carried in a hydrogen atmosphere, chemisorbed hydrogen reacts with positive holes of the lattice, thereby increasing the proton concentration and hence increasing the acidity of the catalyst surface. In this way the isomerisation is increased.

Once the significant role of the non-stoichiometric sulphur in the sulphide catalysts has been established, it is important to elucidate in which step of catalyst preparation the non-stoichiometric sulphur is formed. A WS_2 catalyst as mentioned by Kalechits and Deryagina (43), was prepared in two steps

$$(NH_4)_2WO_4 + 4H_2S \longrightarrow (NH_4)_2WS_4 + 4H_2O$$

$$(NH_4)_2WS_4 + H_2 \longrightarrow 2NH_3 + WS_2 + 2H_2S.$$

In the second step the non-stoichiometric sulphur can be formed in two ways: either

$$(NH_4)_2WS_4 \longrightarrow WS_2 + (NH_4)_2S + S$$

or alternatively reaction of active WS_2 with hydrogen sulphide (either formed during the reaction or added in the case where reductive decomposition is carried out with a hydrogen + hydrogen sulphide mixture). To examine the origin of non-stoichiometric sulphur two catalysts were prepared (43). The first catalyst was prepared by decomposing $(NH_4)_2W^{35}S_4$ with a mixture of hydrogen and hydrogen sulphide and the second sample was prepared by decomposing $(NH_4)_2WS_4$ with a mixture of hydrogen and [^{35}S]-labelled hydrogen sulphide. Both catalysts were investigated for benzene hydrogenation reactions. Hydrogen sulphide formed in the course of hydrogenation reaction as the result of the first reaction contained very little radioactive hydrogen sulphide, while the reverse was true in the second case. The authors believed that the labile, non-stoichiometric sulphur originated from hydrogen sulphide, which was present during the preparation of the catalyst. It was postulated that this sulphur enters the crystal lattice during its preparation and that it can be removed rather easily by hydrogenation.

1.4 Hydrodesulphurisation

The hydrodesulphurisation of petroleum is one of the most widely employed heterogeneous catalytic reactions. It usually involves the use of molybdenum-containing catalysts, commonly cobalt molybdates, as a sulphided mixture of supported cobalt and molybdenum oxide. The current technological emphasis on hydrodesulphurisation of petroleum residues and of coal-derived liquids points to the need for understanding the chemistry of the hydrodesulphurisation of heterocyclic compounds. These are expected to be the least reactive compounds in feed stocks. Thiophene is the simplest compound in this class, and in various studies has been assumed to be representative of the whole class of sulphur-containing aromatic compounds. In consequence, much attention has been given to the elucidation of the kinetic and mechanistic facets of the thiophene hydrodesulphurisation reactions as shown in the reviews by McKinley (46), Schuman and Shalit (47), Schuit and Gates (48), Gates et al.(49) and by Grange (50). Although various mechanisms have been proposed on the basis of results obtained with a variety of catalysts, the exact and true representative mechanism is still uncertain. The fundamental questions which arise concerning hydrodesulphurisation are summarised as follows:-

(a) What is the nature of chemisorbed thiophene?

(b) What is the nature of ring opening: via C-S bond cleavage, ring hydrogenation or intramolecular dehydrogenation?

(c) What is the product distribution: are dienes, diactylenes or tetrahydro thiophene reaction intermediates?

(d) What is the rate of isomerisation of olefinic species?

The most widely discussed mechanism proposed for hydrodesulphurisation of thiophene compounds has been deduced from the studies of the reaction of thiophene itself catalysed by sulphided chromia, cobalt-molybdate and related solids (31-36, 51-53). Amberg and co-workers (32-36, 54) studied the courses of reactions over a variety of catalysts, using mainly the microreactor technique of Emmett and associates (55,56). Owens and Amberg (32) analysed the products from reactions over chromia and supported cobalt-molybdate catalysts at atmospheric pressure, using pulse and continuous flow methods. The product analysis from chromia showed that n-butane, n-butenes and buta-1,3-diene were the only products from thiophene. They came to the following conclusions.

(a) The formation of n-butane is a very slow process as compared to the formation of n-butene from buta-1,3-diene.

(b) The skeletal isomerisation was negligible.

(c) Thermodynamic equilibrium was not attained.

(d) Dehydrogenation was not a significant process under experimental conditions.

The results obtained over cobalt-molybdate were similar to those obtained over chromia catalyst except that no

buta-1,3-diene was found under similar reaction conditions to those used with chromia. The proposed reaction mechanism (32) for the two catalysts is shown in figure 1.5. Preadsorbed hydrogen sulphide had a remarkable poisoning effect on thiophene conversion and almost eliminated n-butene hydrogenation over cobalt molybdate catalyst. A but-1-ene pulse was 93% hydrogenated in the absence of hydrogen sulphide whereas immediately after injection of hydrogen sulphide, the but-1-ene hydrogenation was less than 5% . In each case smaller amounts of hydrogen sulphide caused a smaller change in conversion. However, hydrogen sulphide did not prevent cis - trans isomerisation, double bond shift and the n-butenes were always found to be close to thermodynamic equilibrium proportions, whether they had been produced from thiophene, buta-1,3-diene or one of the n-butenes themselves. In addition hydrogen sulphide did not prevent the total conversion of buta-1,3-diene to n-butene. This implied that the absence of buta-1,3-diene from the thiophene reaction over cobalt-molybdate may have been due to the fact that although it was produced, it reacted too rapidly to survive.

Desikan and Amberg (36) carried out comparative hydrogenation experiments in the presence of sulphided cobalt molybdate catalyst with all sulphur compounds which might be considered as possible intermediates. The main products of tetrahydrothiophene hydrodesulphurisation were n-butenes and n-butane, while n-butyl mercaptan and thiophene were also

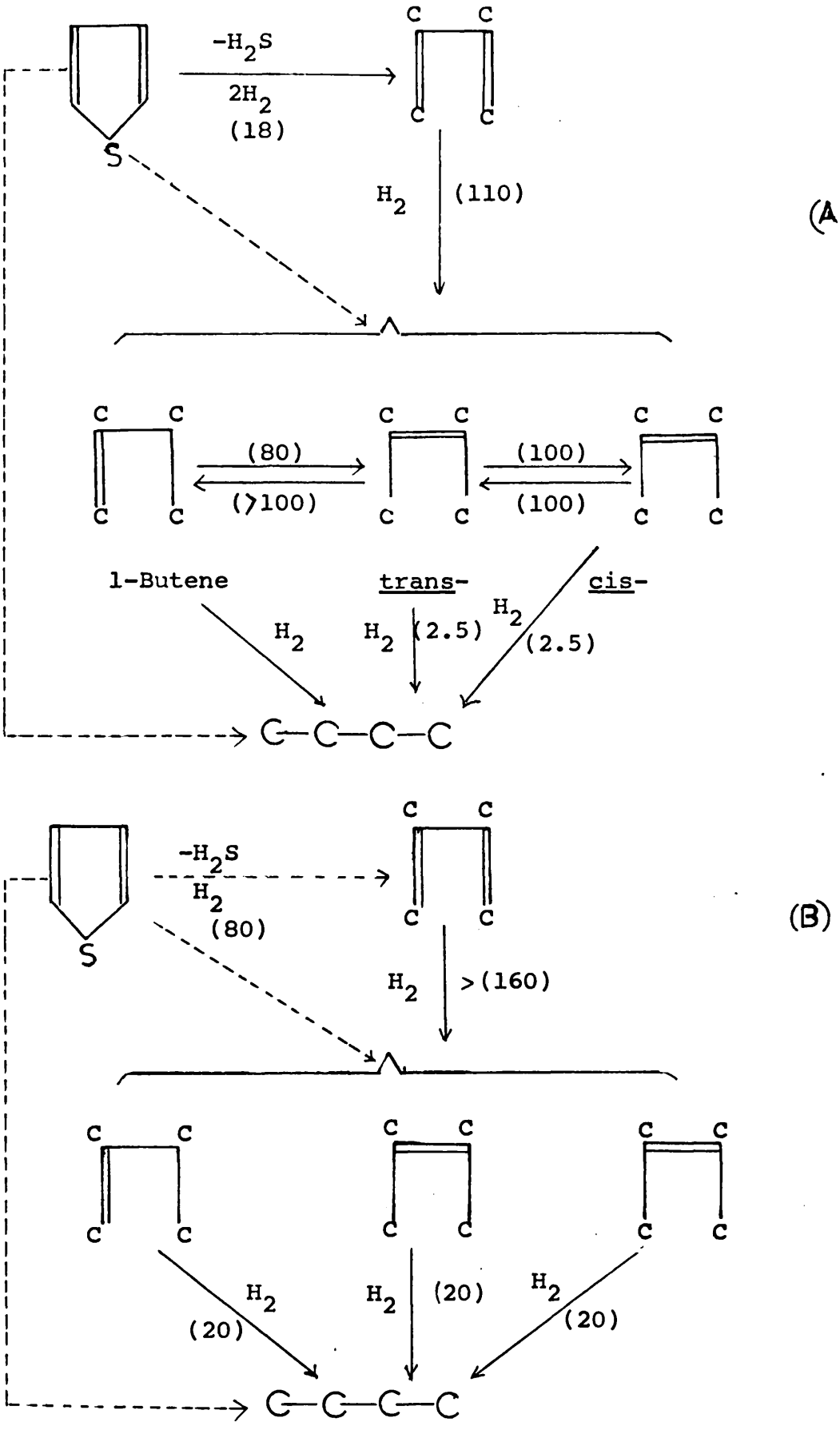


Figure 1.5 Reaction scheme: ⟶ strongly acidic sites; ----> weakly acidic sites; number in brackets indicate reaction rates.

present in the reaction analysis. Comparing with the equilibrium proportions; trans-but-2-ene was the primary product of any reaction, an excess of but-1-ene and cis-but-2-ene was obtained. It was difficult to decide from the distribution alone which of these isomers formed first. However, butanethiol was one of the intermediates in tetrahydrothiophene hydrodesulphurisation (36), which implies that but-1-ene could be the initial isomer produced. Desikan and Amberg (36) also attempted to find out whether desulphurisation and hydrogenation occur on the same or different sites. It was found that alkali hydroxides decrease both reactions, proving thereby that two reactions take place on acid catalyst centres. Desikan and Amberg on the basis of their detailed studies of pyridine poisoning coupled with some other poisoning work (57,58,59) proposed a two-site theory. According to these workers the reaction takes place on two types of acid sites, one very strongly acidic and the other having low affinity for electrons. It is on the strong acid sites that olefins are hydrogenated. Hydrogen sulphide, thiophene and pyridine are strongly adsorbed on these sites, deactivating them for olefin hydrogenation. The desulphurisation takes place on the weakly acidic sites which can only be deactivated by strongly basic substances.

The reaction scheme which refers to the two main sites is given in figure 1.6. It is a qualitative summary of a great many experiments the extent to which some of the steps occur very much depending on reaction conditions and the state of the catalyst.

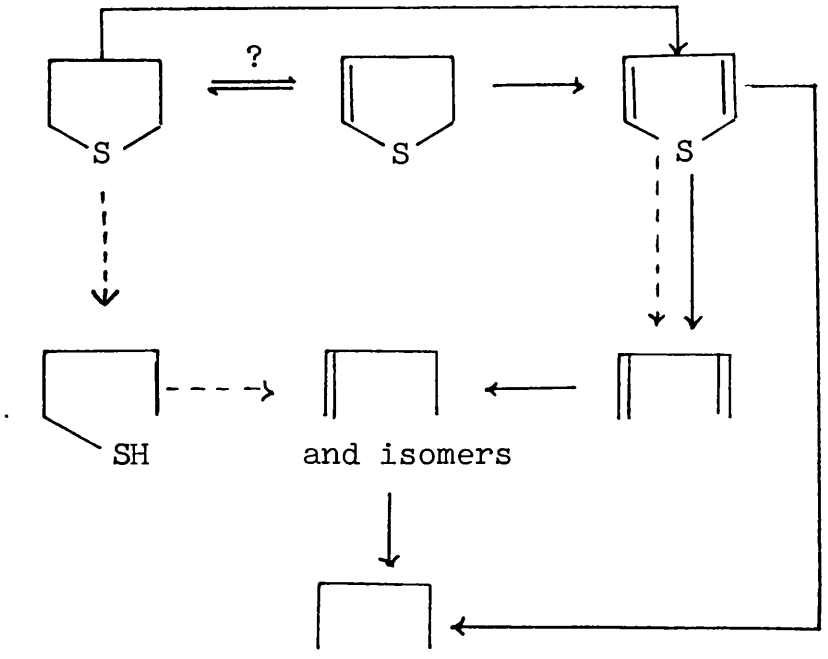


Figure 1.6 Reaction scheme and catalytic sites

Legends: ⟶, strong acid sites;

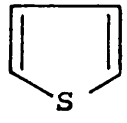
⇢, weak acid sites

?, route not definitely identified.

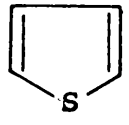
The two sites concept achieved further support in later studies carried out by Smith et al. (60) of the deuterium-thiophene hydrodesulphurisation reactions. Pazos and Andréu (61) were, however, able to indicate the presence of three different kinds of sites on cobalt-molybdenum catalysts involved in hydrodesulphurisation reactions: desulphurisation, aromatic hydrogenation and olefin saturation sites. They proposed their mechanism for thiophene reaction on the basis of the products obtained. In addition to the usual products,

they also observed tetrahydrothiophene, mercaptans and sulphides as intermediates.

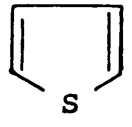
The exchange reactions between thiophene and deuterium have been studied using MoS_2 and WS_2 as catalysts (62). The following reactions were observed to occur:



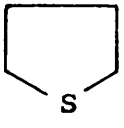
$$+ 3H_2 \longrightarrow C_4H_8 + H_2S$$



$$+ 4H_2 \longrightarrow \underline{n}\text{-}C_4H_{10} + H_2S$$



$$+ 2H_2 \longrightarrow$$



Similar reactions were observed with tetrahydrothiophene over WS_2. The decomposition of tetrahydrothiophene over MoS_2 was accompanied by the formation of buta-1,3-diene, which rapidly hydrogenated to form n-butenes.

In a recent publication Christopher et al. (63) described a study of thiophene-deuterium exchange reactions, in which the products were analysed by mass-spectrometry and microwave spectroscopy. They were able to conclude that sites present on unsupported MoS_2, being responsible for olefin hydrogenation, isomerisation and hydrodesulphurisation activity were also present on the sulphided Co-Mo/Al_2O_3.

Lipsch and Schuit (31) proposed a somewhat different mechanism in which the major part of the desulphurisation activity of the cobalt-molybdenum catalyst is due to MoO_3, the active centre being located on sites of an "independent" Mo----O bond. The authors assumed one-point adsorption of thiophene by the formation of a S-Mo bond on an anion vacancy. Hydrogen sulphide, n-butenes and water are adsorbed on the same vacancy. This may provide an explanation of the deactivating effect of these substances on desulphurisation and hydrogenation of the n-butenes. Thiophene is known to bind more strongly than n-butenes or hydrogen sulphide and has, therefore, a stronger deactivation effect upon the n-butene hydrogenation. The proposed steps in Lipsch and Schuit mechanism were as follows:

(a) Thiophene is adsorbed on an anion vacancy formed by reduction of MoO_3 and a S-Mo bond is established.

(b) A hydrogen atom from a neighbouring OH group is transferred to the adsorbed molecule of thiophene, and a C - S bond is broken.

(c) A second hydrogen atom attacks the adsorbed thiophene and the second C - S bond is broken.

(d) Buta-1,3-diene either desorbs (in agreement with Kolboe and Amberg (54)) or it may undergo hydrogenation either on the same site or on other sites.

(e) The original sites are regenerated by the reaction with two hydrogen atoms and the formation of hydrogen sulphide which is then desorbed.

A similar mechanism was assumed for sulphided catalysts where MoO_3 is reduced to the "sulphidic" form (31) as shown below.

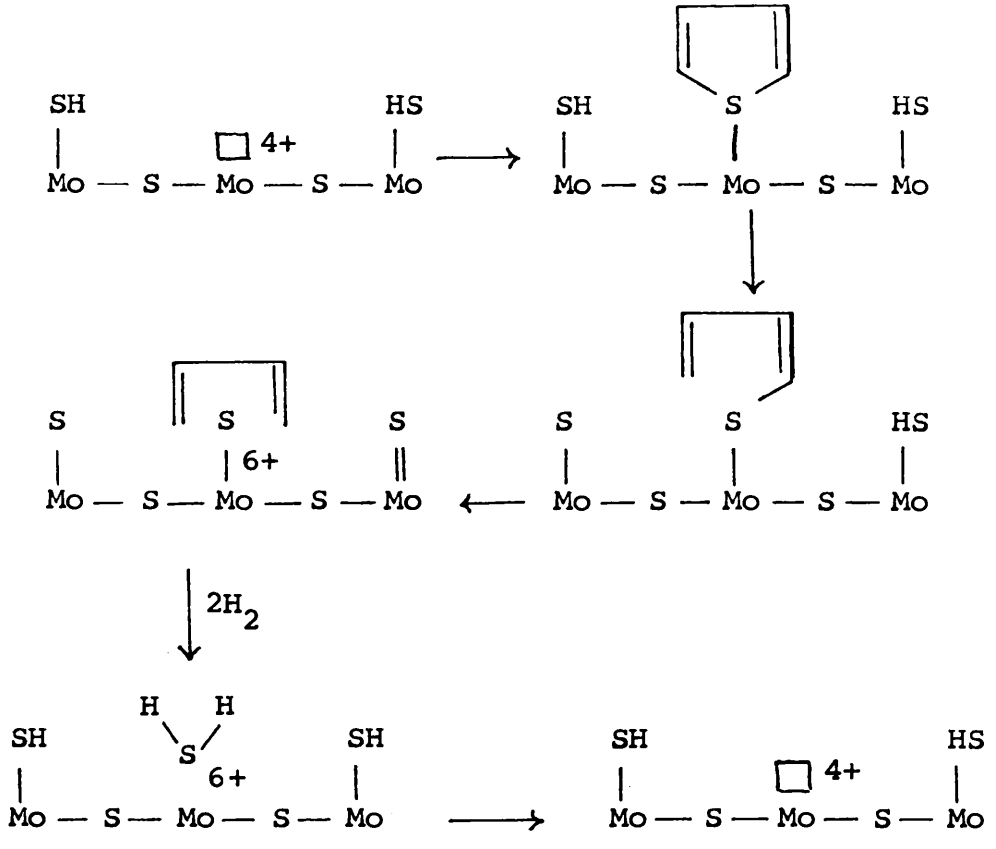


Figure 1.7 The suggested one-point mechanism of thiophene hydrodesulphurisation on sulphided and related catalysts.

On the other hand Kolboe (54, 64) suggested on the basis of one-point adsorption that dehydrodesulphurisation is the actual route instead of hydrodesulphurisation (figure 1.8), where hydrogen sulphide is removed by β-elimination. Infrared studies (24) and deuterium tracer experiments by Mikovsky et al. (65) have provided support for Kolboe's mechanism.

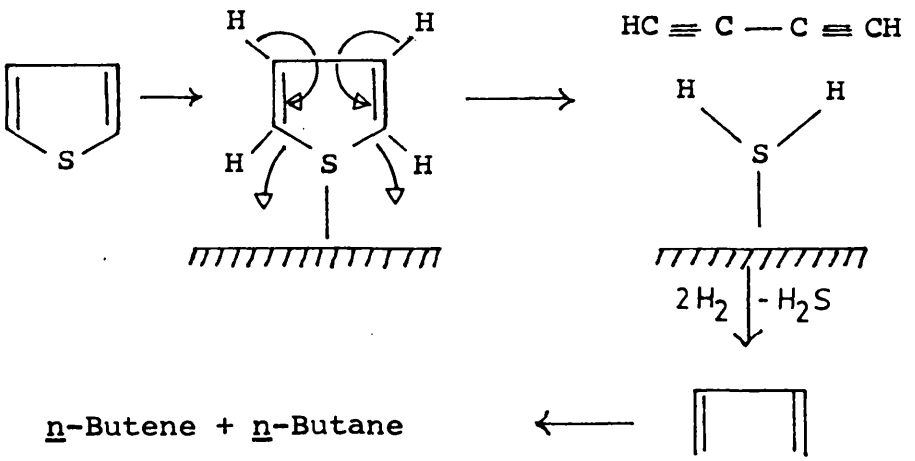


Figure 1.8 "One-point" mechanism for hydrodesulphurisation of thiophene

The main objection to the one-point model arises from the kinetic data. The results obtained over sulphided Co-Mo/Al_2O_3 at 300^{o}C and at 100 atm. pressure and interpreted by Kwart and Schuit (66) show that benzothiophene is ten times more reactive that 4,6-dimethyldibenzothiophene, but only two times more reactive than 4-methylbenzothiophene. Similar reactivity patterns were observed at subatmospheric pressure (67).

Desikan and Amberg (35,36) stated that the hydrodesulphurisation of 2-methyl- and 3-methylbenzothiophene takes place over sulphided Co-Mo/Al_2O_3 catalysts with indistinguishable apparent activation energies. The low pressure data for benzothiophene and its methyl substituents (68) show that 3-methylbenzothiophene is slightly less reactive than 2-methylbenzothiophene, whereas on steric grounds the order should be in reverse, if the one-point model of adsorption is accepted. These results led Kwart and his co-workers to propose their "multi-point" adsorption model for thiophenic compounds (66). They proposed that the C_1— C_2 bond of the thiophene compound is coordinated at an anion vacancy of the catalyst, whilst the sulphur atom interacts with the sulphur of the surface, resulting in a change in electron distribution in the thiophene ring. These changes facilitate the addition of a hydrogen atom to the C_1— C_2 centre with the formation of dihydrogenated thiophene. Figure 1.9 shows the proposed three-point adsorption model for thiophene (the broken and wavy lines represent weaker interactions and longer/remote bonds respectively between the centres). From this three-point adsorbed model, several alternative routes for product forming steps can be constructed (figure 1.10).

Now if partial hydrogenation occurs as depicted in (A), electron delocalization from the partial covalency to the proton at C_2 will result in the S—C_1 bond breaking and (A) will then be converted to (B). If partially bonded protons in

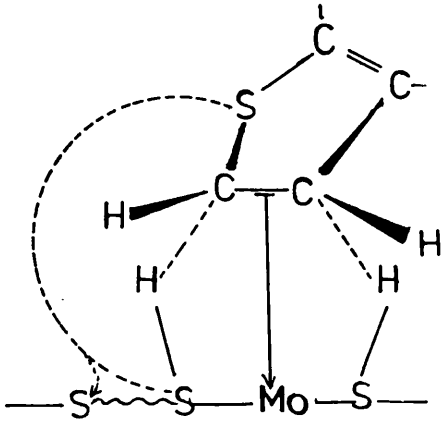


Figure 1.9 Proposed structure of chemisorbed thiophene in three-point mechanism.

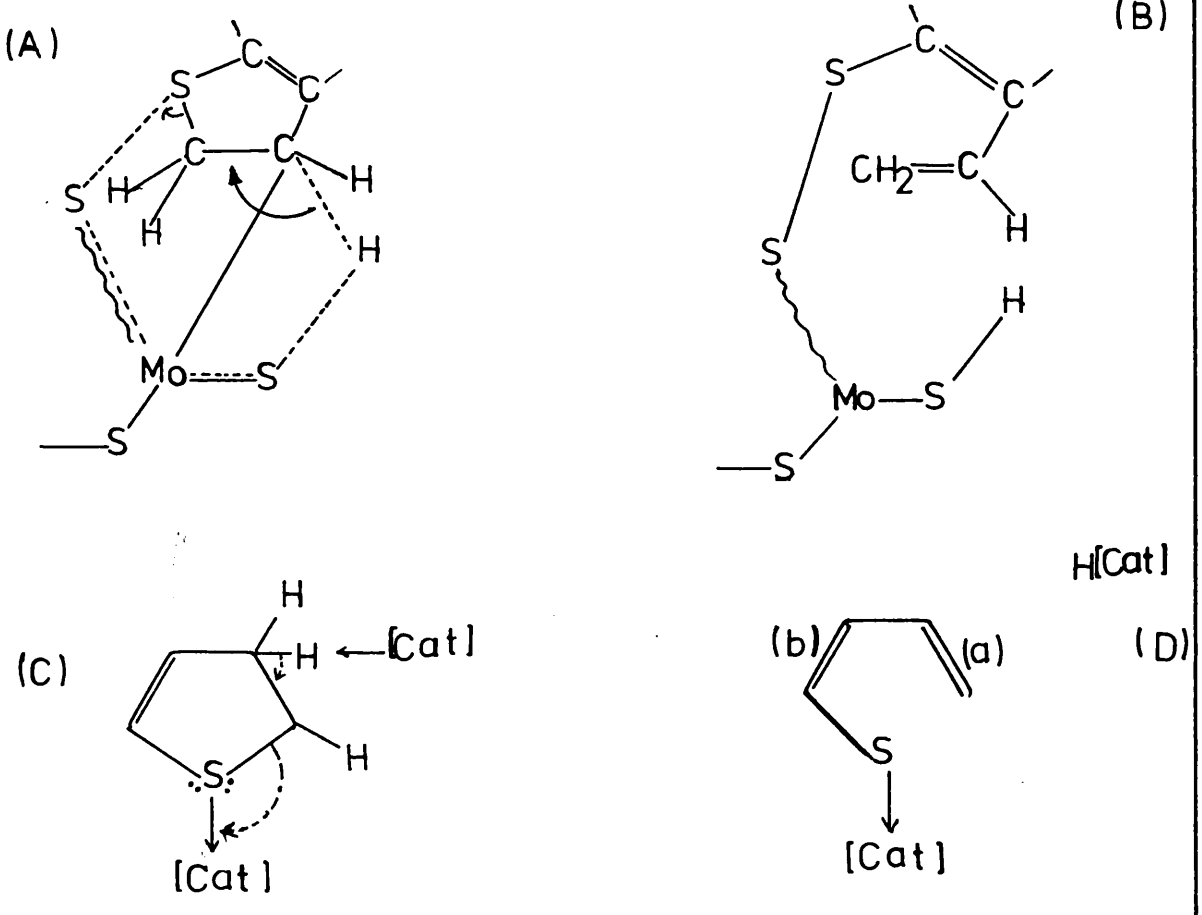


Figure 1.10 Different routes for product forming steps from adsorbed thiophene.

the figure 1.9 are involved in the formation of covalent bonds to C_1 and C_2 by a concerted process, then the hydrothiophene (C) is no longer aromatic. The structure (C) is highly susceptible to thermal β-elimination. The structure (D) which is presumably strongly bonded to the catalyst, can undergo chemisorption of its olefinic groups to Mo^{4+} at anion vacancies created by hydrogenation and desorption of hydrogen sulphide. This will result in breaking of the C—S bond. By this process buta-1,3-diene will be liberated, or if the more remote double bond (a) is reduced before the other double bond (b), then n-butene will be produced directly instead of buta-1,3-diene.

1.5 The hydrogenation of unsaturated hydrocarbons in the presence of sulphide catalysts

1.5.1 Introduction

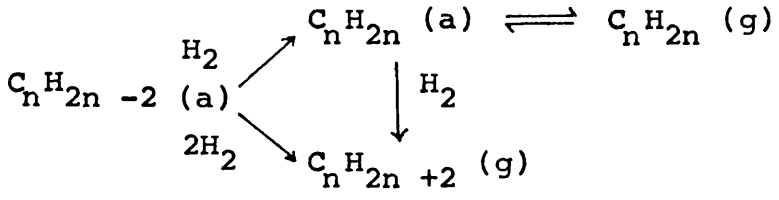
Sulphide catalysts are widely used in industry, especially in the hydrodesulphurisation of petroleum fractions, hydrocracking and hydroprocessing. Petrochemicals manufacturing and petroleum processing which consume olefinic hydrocarbons operate more efficiently when the reactor charge is relatively free of diolefins. Buta-1,3-diene is a particularly undesirable diolefin, which often contaminates the butene fraction fed to petroleum processing. Therefore to effect the removal of buta-1,3-diene a catalyst with a high activity for diolefin hydrogenation but a low hydrogenation activity for butene

hydrogenation is required (59). The use of sulphide catalysts for the hydrogenation of unsaturated hydrocarbons of this type has been receiving attention during the past few years.

The gas phase hydrogenation of buta-1,3-diene has been studied in detail by Bond, Wells and Webb et al. over noble metals (69-72). The reactions between hydrogen and deuterium and buta-1,3-diene and olefins over semi-conductor metal oxide catalysts has been studied by a few researchers (73-78). In spite of the abundant literature available on the catalysis of unsaturated hydrocarbons on metals and related catalysts, relatively few studies have been carried out using sulphide catalysts. Most of the available data for sulphide catalysts is related to Ni_3S_2 and MoS_2. The research group of Tanaka is extensively involved in investigating the relationship between the intermediates of hydrogenation reactions of unsaturated hydrocarbons and the configuration of active sites over Ni_3S_2 and MoS_2 catalysts (79-88). The details of these investigations are worth mentioning and are described in section 1.5.3.

1.5.2 Selectivity

Consider the following reaction scheme



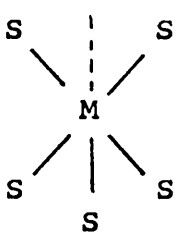
which will elucidate the term selectivity. The selectivity is used to denote the extent to which diunsaturated hydrocarbon will yield alkene as opposed to alkane; thus the selectivity,

$$S = \frac{\text{yield of olefin}}{\text{yield of olefin + paraffin}} .$$

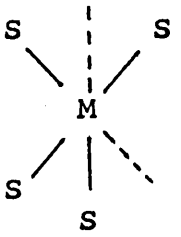
It is possible to induce selectivity by partially poisoning the metal catalysts by sulphur or sulphur containing compounds, for example, selective hydrogenation of iso-prene to iso-pentene (89) and buta-1,3-diene to n-butene can be achieved using a partially sulphided nickel catalyst (90). Selectivity was modified when cobalt and nickel (91) and rhenium (92) contaminated with sulphur were used to study but-1,3-diene hydrogenation reactions.

1.5.3 Hydrogenation and isomerisation controlled by the coordinative unsaturation of active sites on sulphide catalysts

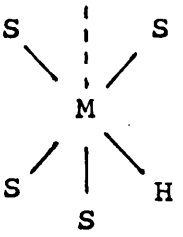
Siegel (92) predicted the configuration of active sites on oxide catalysts in relation to the configurational prerequisite in homogeneous catalysis. The sites on sulphides or on oxides can be described according to the degree of coordination unsaturation as follows:



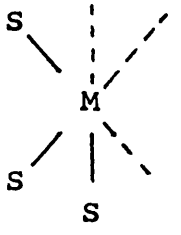
(A)



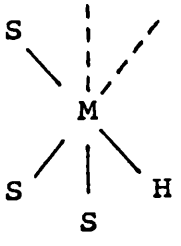
(B)



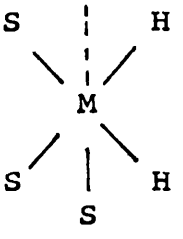
(BH)



(C)



(CH)



(CH_2)

The MoS_2 has a hexagonal structure characterised by a sandwich-like layer form. If the stoichiometric crystallite is cleaved along the C-axis, various molybdenum ions are exposed on the newly formed surface along which 4-coordinated

molybdenum ions, the B-sites, are one of the most feasible sites. Furthermore, the B-site at the crystallite corner has a sulphur atom which is singly bonded to molybdenum ion and which may be easily removed by evacuating at high temperature. In fact, there are two kinds of active sites on the evacuated MoS_2 surface, which may correspond to the B- and C-sites (83). The sulphur atoms in the MoS_2 are not so mobile that the C-sites, as well as the B-sites formed by evacuation, remain on the surface. The surface concentration of B-sites is much greater than that of the C-sites, the latter are preferentially formed at the crystallite corners. These surface sites are responsible for catalytic hydrogenation and isomerisation and/or the hydrogen exchange of olefins (83). The hydrogenation exchange of olefins and isomerisation reactions are very slow over MoS_2 and are markedly enhanced by the addition of hydrogen. The remarkable hydrogen promoting effects on isomerisation and with the hydrogen exchange of olefins may indicate the formation of half-hydrogenated intermediates on the B-type sites in the presence of hydrogen. Evidence for the two different active sites on MoS_2 has been obtained in the reaction of n-butene with deuterium. The isomerisation was promoted to a remarkable extent by the addition of deuterium, although very few deuterium atoms were present in the isomerised product. More than 90 per cent of the products were d_o-butenes, whilst, simultaneously formed n-butane was 80 per cent d_2-butane. These results suggested that the d_2-butyl

intermediate exists in the hydrogenation on the C-type sites and d_o-butyl intermediate in isomerisation prevails on the B-type sites (figure 1.11).

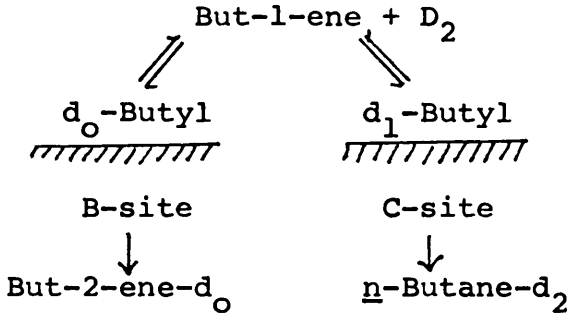


Figure 1.11 The half-hydrogenated intermediates on B-sites and on C-sites.

The hydrogen sulphide treated MoS_2 catalyst showed somewhat diminished activity (94). If the different degrees of coordinative unsaturation of active sites are related with different catalytic activities, then one might expect one of the sites to be diminished preferentially by hydrogen sulphide treatment. Therefore C-sites may be reduced to B-sites and/or to A-sites. The hydrogenation of ethylene on hydrogen sulphide treated MoS_2 catalyst suggests that this is the case (94).

The idea that isomerisation of olefin proceeds through half-hydrogenated intermediate on BH-sites, cannot explain the double bond migration of 2-methylbut-1-ene on MoS_2 catalyst (85). When a mixture of 2-methylbut-1-ene and

cis-but-2-ene was admitted to the MoS_2 catalyst at room temperature, there was a rapid double bond migration in 2-methyl-but-1-ene, whilst no appreciable isomerisation of cis-but-2-ene occurred. On the other hand, when hydrogen was added to the reaction mixture, the isomerisation of cis-but-2-ene was rapidly enhanced, but there was no appreciable change in the double bond migration of 2-methylbut-1-ene. This behaviour of 2-methylbut-1-ene double bond migration was attributed to tertiary carbonium ion formation on the MoS_2 catalyst. To investigate whether iso-butene is also present as a carbonium ion on MoS_2, the possibility of a hydrogen exchange reaction between iso-butene-d_o and iso-butene-d_8 was undertaken. The hydrogen exchange reaction was very slow in the absence of hydrogen, but was markedly enhanced by the addition of hydrogen. On the basis of these facts, Okuhara et al. (85) suggested that the carbonium ion formation is feasible for 2-methylbut-1-ene but not for iso-butene and/or other olefins on MoS_2. The types of intermediates proposed for the hydrogen exchange and/or isomerisation reactions on MoS_2 are shown in the following table.

Table 1.1

Intermediates for the hydrogen exchange reaction and/or isomerisation reaction on MoS_2 catalyst

Reaction	Intermediate
Propene	σ-Alkyl
But-1-ene	σ-Alkyl
iso-Butene	σ-Alkyl
3-Methylbut-1-ene	σ-Alkyl
2-Methylbut-1-ene	carbonium ion.

1.5.4 Intermediates on the active sites of MoS_2 with different coordinative unsaturation

We have discussed in the previous section that the isomerisation and the hydrogen exchange reaction between olefins are markedly increased on MoS_2 catalyst, when a small quantity of hydrogen is added to the reaction mixture. Systematic studies were made by Okuhara et al. (86) to investigate the nature of intermediates formed on the BH-sites during the isomerisation or hydrogen exchange reactions of olefins. In an experiment the coisomerisation of cis-but-2-ene-d_o and cis-but-2-ene-d_8 (1:1) was carried out at room temperature on MoS_2 catalyst in the presence of hydrogen. The reaction products were then subjected to microwave spectroscopic analysis. The results indicate that the cis -

trans isomerisation reaction occurs only with a stereo-specific hydrogen addition (A) and elimination (E) mechanism on BH-sites (figure 1.12). In addition to this, nearly 100 per cent cis-but-2-ene-2-d_1 was formed in coisomerisation reaction which verifies that an iso-butyl species was a reaction intermediate.

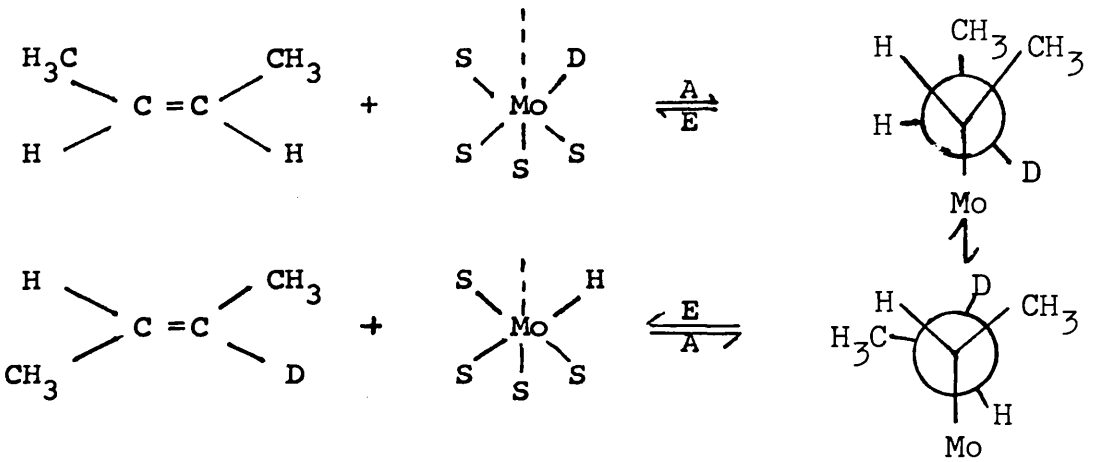


Figure 1.12 Stereospecific addition and elimination of hydrogen to cis-but-2-ene on MoS_2 catalyst.

In contrast to but-2-ene, the intermolecular exchange of vinyl hydrogens of α-olefins, such as propene and but-1-ene, occurred much more rapidly than the double bond migration on MoS_2, although the exchange between deuterium and the olefin was very slow at room temperature. In order to find the intermediate involved in such a rapid exchange reaction, the exchange reaction between but-1-ene-d_o and but-1-ene-d_8, and between propene-d_o and propene-d_6 was performed; and the

resulting d_1-species were analysed by microwave spectroscopy. The data suggests that the rapid hydrogen exchange in α-olefins involves only their vinyl hydrogen. It is interesting to note that the ratio of propene-1-d_1 to propene-2-d_1 as well as but-1-ene-1-d_1 to but-1-ene-2-d_1 were approximately $^3/_7$, which implies that the n-alkyl intermediate was about 70 per cent and 30 per cent iso-alkyl intermediate for the hydrogen exchange reaction of α-olefins on BH-sites of MoS_2 catalysts.

It has been shown earlier that the cis - trans isomerisation of but-2-ene on MoS_2 proceeds through an iso-butyl intermediate. However, the double bond migration of but-1-ene occurring through the iso-butyl intermediate is extremely slow as compared with cis - trans isomerisation. This phenomenon suggests that the iso-butyl formed from but-1-ene (iso-butyl I) and from but-2-ene (iso-butyl II) should be distinguishable on BH-sites of MoS_2. This can be explained by the restricted rotation of the adsorbed iso-butyl intermediates (figure 1.13). The rapid exchange of vinyl hydrogens and cis -trans isomerisation proceeds without the rotation around Mo-C bond which is required by the double bond migration reaction. Such unusual restricted rotation of σ-alkyl adsorbed intermediates formed on the MoS_2 catalyst was thought to be a consequence of the structure of MoS_2, with an edge surface of the sandwich-like crystallite on which BH-sites exist.

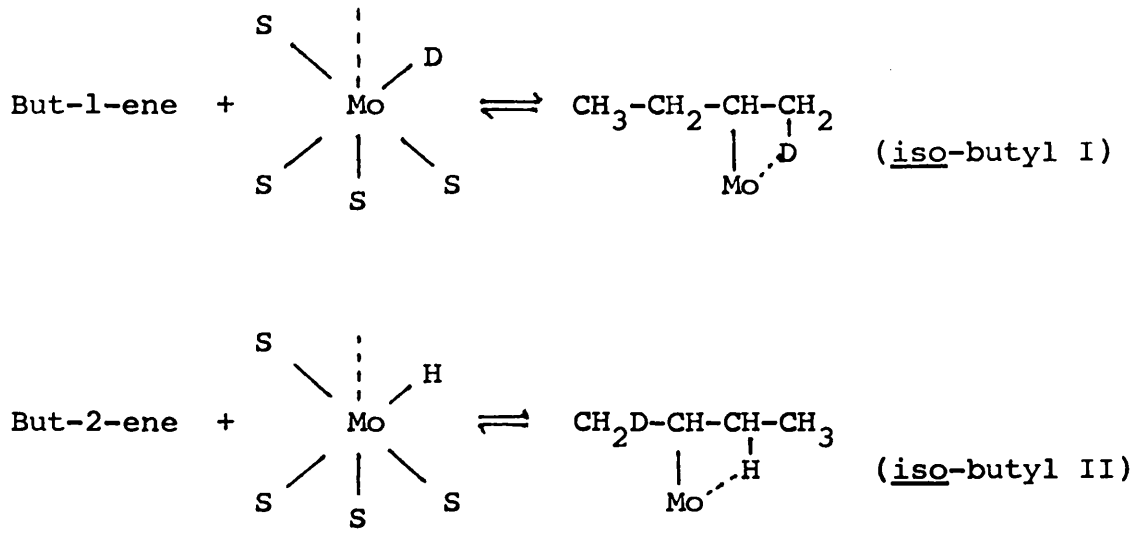


Figure 1.13 The restricted rotation of the adsorbed iso-butyl intermediates on MoS_2 catalyst.

1.5.5 Hydrogenation of buta-1,3-diene on molybdenum disulphide catalyst

Hydrogenation of buta-1,3-diene in the presence of MoS_2 has been studied by Okuhara et al. (84,87,88,95) using deuterium as a tracer. The intermediates of the hydrogen exchange reactions were analysed by microwave spectroscopy. The reaction of buta-1,3-diene with deuterium was studied on MoS_2 catalyst (84) and the but-1-ene-d_2 was identified as 3,4-d_2-but-1-ene. The exchange reaction of buta-1,3-diene and deuterium proceeded simultaneously and buta-1,3-diene-d_1 and hydrogen deuteride was formed. The hydrogenation reaction

of buta-1,3-diene with a mixture of hydrogen and deuterium on MoS_2 resulted in the formation of but-1-ene-d_o and but-1-ene-d_2 and a small amount of but-1-ene-d_1 in the initial stages of the reaction. In another experiment (84), it was confirmed that isotopic mixing between buta-1,3-diene-d_o and buta-1,3-diene-d_6 was markedly enhanced by adding hydrogen. This suggests that the associative mechanism for hydrogen exchange reaction of buta-1,3-diene was operative, that is, the exchange reaction proceeded via a half-hydrogenated intermediate.

If the exchange reaction between buta-1,3-diene and deuterium occurs on CH_2-sites, the position of the deuterium atom in buta-1,3-diene-d_1 molecule provides an important clue as to whether the intermediate for hydrogen exchange reaction is a n-butenyl or an iso-butenyl(σ-allyl) species as shown in figure 1.14.

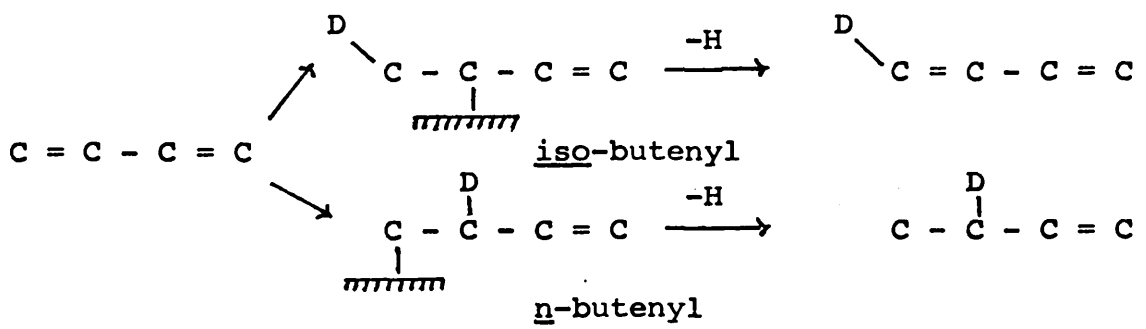


Figure 1.14 Formation of iso-butenyl and n-butenyl intermediates in the hydrogenation reaction of buta-1,3-diene over MoS_2

In order to determine the deuterium atom position in the buta-1,3-diene, the reaction containing buta-1,3-diene-d_1 was stopped at a certain conversion and then hydrogenated to butene with hydrogen on MoS_2 catalyst. This method resulted in little hydrogen scrambling of the buta-1,3-diene and hence the position of the deuterium atom was maintained in the product but-1-ene-d_1. Microwave spectroscopic analysis showed that the deuterium atom was located on the terminal carbon atom (51 per cent but-1-ene-4-d_1 and 49 per cent but-1-ene-1-d_1). This shows that the iso-butenyl species is an intermediate for the hydrogen exchange reaction. The iso-butenyl form is preferred to the n-butenyl form on CH_2 sites, provided that both the exchange reaction and the hydrogenation take place on a common half-hydrogenated intermediate. However, the intermediate of the hydrogenation reaction is not necessarily identical with that of the exchange reaction. A new method was proposed to elucidate the intermediate of hydrogenation reaction (95). Using this method, a hydrogen deuteride molecule when added to buta-1,3-diene gives two geometrical isomers according to its orientation in the addition reaction and to the nature of the reaction intermediate. The reaction scheme can be depicted as shown in figure 1.15.

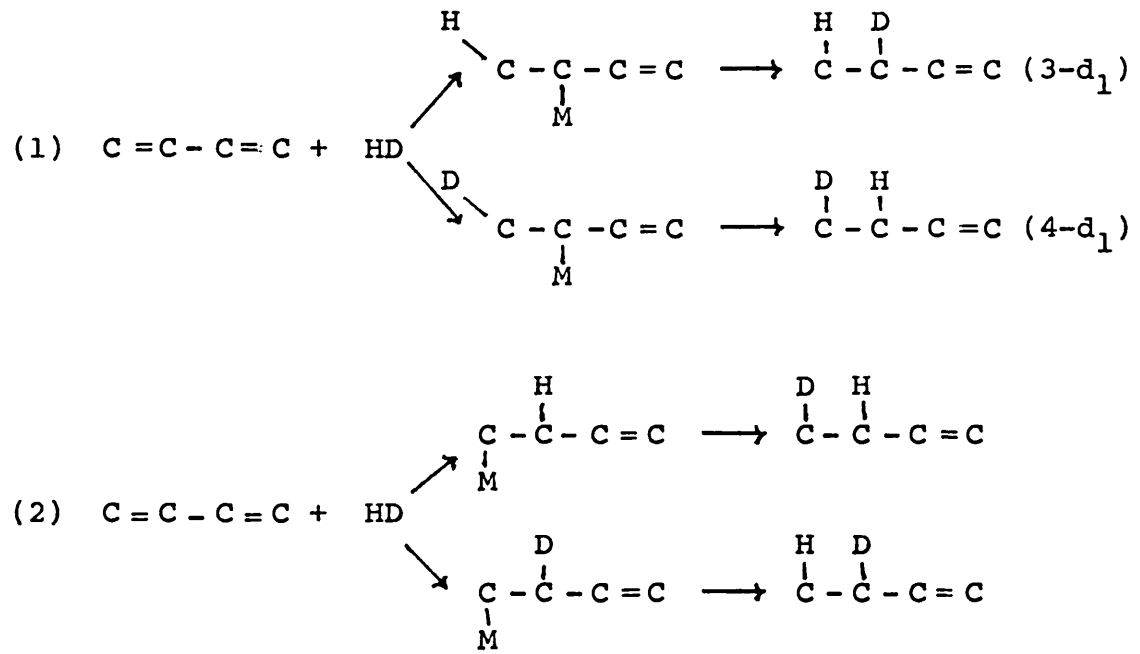


Figure 1.15 Addition of hydrogen deuteride molecule to buta-1,3-diene in the presence of MoS_2 catalyst

In each case the selectivity to give either of the two isomers is decided whether a hydrogen atom is added first or a deuterium atom. If <u>iso</u>-butenyl is the intermediate, but-1-ene-3-d_1 formation may be expected to prevail over but-1-ene-4-d_1 in accordance with the isotopic effect at the first step. Accordingly, if the reaction occurs through the <u>n</u>-butenyl intermediate, then but-1-ene-4-d_1 will be expected. These pieces of information suggest that the hydrogenation of buta-1,3-diene and the hydrogen exchange between buta-1,3-diene and deuterium proceed via an identical half-hydrogenated intermediate, <u>iso</u>-butenyl, on CH_2-sites. Furthermore, nearly 100 per cent selectivity to but-1-ene is indicative of little possibility of the conversion of σ-allyl to π-allyl complex on the active sites.

CHAPTER 2

2. THE OBJECTIVE OF THE PRESENT WORK

The following studies were undertaken to investigate the catalytic properties of molybdenum disulphide;

(a) the reaction of buta-1,3-diene with hydrogen;

(b) the influence of sulphur upon the catalytic properties of molybdenum disulphide for the hydrogenation of buta-1,3-diene;

(c) the reaction of thiophene with hydrogen;

(d) the adsorption studies of hydrogen sulphide over molybdenum disulphide catalyst.

The reaction of buta-1,3-diene with hydrogen were studied with the following aims;

(i) to study the butene distribution as a function of reaction conditions;

(ii) to study the kinetic features of the reaction;

(iii) to elucidate mechanism of reactions.

The influence of sulphur upon the catalytic properties of molybdenum disulphide catalysts for the hydrogenation of buta-1,3-diene was studied with the following aims;

(i) to study the influence of sulphur (sulphur introduced either by carrying out thiophene hydrodesulphurisation reactions or by catalyst exposure to hydrogen sulphide) upon the butene distribution and the hydrogenation activity;

(ii) to study the variation of butene distribution as a function of sulphur uptake;

(iii) to study the kinetic facets of the reactions;

(iv) to attempt to establish the mechanism for the formation of but-1-ene and but-2-ene, that is whether but-2-ene is produced by (a) direct 1,4 addition of hydrogen to adsorbed but-1,3-diene or (b) by 1,2 addition to the buta-1,3-diene and subsequent isomerisation.

Thiophene hydrodesulphurisation studies were undertaken with the following aims;

(i) to determine the distribution of reaction products;

(ii) to measure the selectivity as a function of reaction conditions;

(iii) to compare the catalytic behaviour of molybdenum disulphide, when sulphur was introduced via hydrodesulphurisation of thiophene with the catalyst which was treated with hydrogen sulphide.

CHAPTER 3

3. EXPERIMENTAL

3.1 Materials

3.1.1 Hydrogen

Cylinder hydrogen (British Oxygen Co.) was purified by passage over a reduced 5% Pd/WO_3 catalyst at room temperature to remove traces of oxygen and then through a magnesium perchlorate trap to remove water vapour.

3.1.2 Hydrogen sulphide

Hydrogen sulphide was supplied by BDH Laboratory Chemicals Ltd. and was quoted as being 99.7% pure. It contained no impurities detectable by gas chromatography, and was merely degassed before use.

3.1.3 Radioactive hydrogen sulphide

[^{35}S]labelled hydrogen sulphide was supplied by the Radiochemical Centre, Amersham, with specific activity of 5mCi. It was diluted to the required specific activity with inactive hydrogen sulphide before use.

3.1.4 Buta-1,3-diene

(99% purity BDH Laboratory Chemicals Ltd.) was found to contain no impurities detectable by gas chromatography and was used after degassing several times.

3.1.5 The butenes

Chemically pure grade, trans-but-2-ene (Matheson Co. Inc.) contained no impurities detectable by gas chromatography and was merely degassed before use. Similarly but-1-ene and cis-but-2-ene, both supplied by Air Products Ltd., were found to contain no detectable impurities and were used after degassing.

3.1.6 Thiophene

Thiophene was supplied by BDH Laboratory Chemicals Ltd. and was quoted to contain not more than 0.2% carbon disulphide. It was degassed several times before use.

3.2 The preparation of catalyst

The catalyst, molybdenum disulphide, was prepared by dissolving about 110g of ammonium molybdate (Analar), $(NH_4)_6Mo_7O_{24}.4H_2O$, in 400ml 36%w/w ammonia solution at about 65°C. On passing hydrogen sulphide through this warm solution of ammonium molybdate, the colour gradually changed to dark red and eventually red crystals of ammonium thiomolybdate $((NH_4)_2MoS_4)$ were precipitated. The hydrogen sulphide treatment was continued for about half an hour. The ammonium thiomolybdate crystals were filtered off and dried for 48 hours before being calcined in a muffle furnace, under a flowing nitrogen atmosphere, at 1000°C for about 5 hours. The furnace was subsequently allowed to cool to room temperature over

approximately two hours with the catalyst maintained under a nitrogen atmosphere.

3.3 Apparatus

3.3.1 The vacuum system (see figure 3.1)

The apparatus consisted of a conventional high vacuum system, which was evacuated by a mercury diffusion pump (P_2), backed by a rotary oil pump (P_1). A vacuum of 10^{-4}torr or better was maintained in the system. Five storage vessels, V_1 - V_5, contained hydrogen, buta-1,3-diene, thiophene, hydrogen sulphide, and [^{35}S]-hydrogen sulphide respectively. Another vessel V_6 was connected to storage vessel V_5 to facilitate the dilution of [^{35}S]-hydrogen sulphide. The vessels were connected to high vacuum line a - a^1.

An ampoule of [^{35}S]-hydrogen sulphide (A) was sealed onto the vacuum line adjacent to storage vessel V_5.

A cylindrical Pyrex reaction vessel of capacity ca. 100cm^3 was connected to the system via a B7 cone and socket. The catalyst rested on the bottom of the reaction vessel. Reactions were monitored by measuring the pressure change recorded on the mercury manometer (M), during the course of the reaction. The vacuum system incorporated a mixing vessel (MV) in which mixtures of the reactants, of the required composition, were stored. An expansion vessel (EV) was used for the extraction of the products which were then freed from unreacted hydrogen by being pumped through the spiral trap

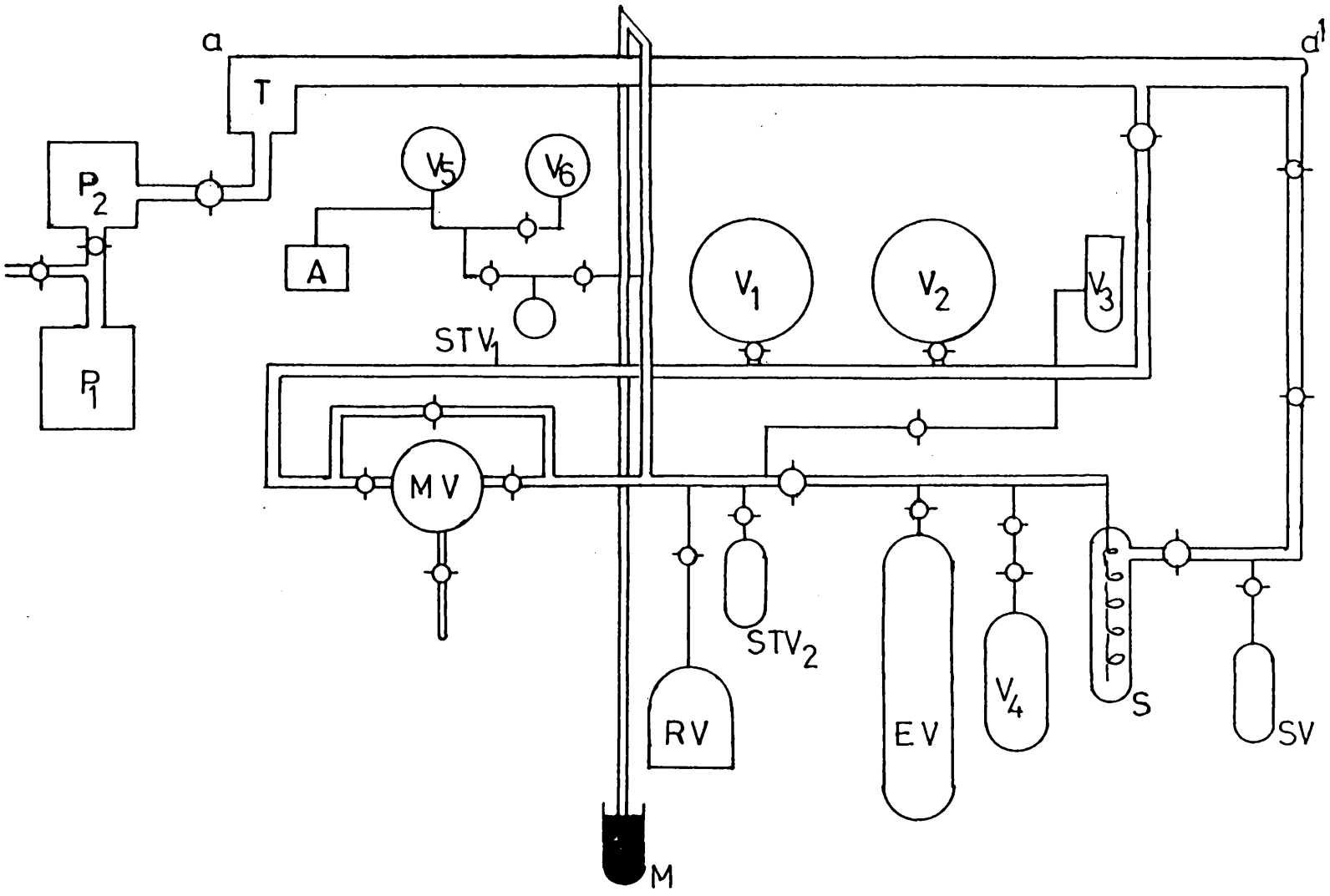


Fig 3·1 The Vacuum System

(S), which was cooled in liquid nitrogen. The products were then distilled from the spiral trap into a liquid nitrogen cooled sample vessel (SV) for transfer to the chromatography system for analysis.

3.3.2 Experimental procedure

In each series of reactions, the required weight of catalyst, usually 500mg, was sealed into the reaction vessel which was then connected to the vacuum system. The catalyst was evacuated for 30 minutes at room temperature, after which the temperature was raised to 350^{o}C by means of an electric furnace surrounding the reaction vessel, with the catalyst maintained under vacuum. The current supplied to the furnace, and hence the temperature, was controlled by the use of a Variac transformer. Temperatures were measured using a 'Comark' electronic thermometer which utilised a chromium/aluminium thermocouple, whose hot junction was placed in contact with the base of the reaction vessel.

Reactions were carried out by admitting a suitable pressure (150torr) of reaction mixture to the reaction vessel, and measuring the pressure fall on the manometer at various intervals of time. After a pressure fall corresponding to the desired extent of reaction, the products were extracted for analysis.

3.4 The gas chromatography system

3.4.1 The apparatus

A block diagram of the gas chromatography system is shown in figure 3.2. A column (A) was constructed which could separate the products of the hydrogenation of buta-1,3-diene, these being n-butane, but-1-ene, trans-but-2-ene cis-but-2-ene and buta-1,3-diene. This consisted of 33% w/w dimethylsulpholane supported on 30 - 60 mesh firebrick. The column which was 12m long was constructed from 6mm i.d. glass tubing.

In order to separate products of thiophene hydrodesulphurisation, namely n-butane, but-1-ene, trans-but-2-ene, cis-but-2-ene, hydrogen sulphide, propane and thiophene an alternative column was required, since column (A) could not resolve hydrogen sulphide and trans-but-2-ene. A suitable system was found by employing two columns in series. These consisted of a 5m long, 6mm i.d. glass column (B) packed with 33% w/w dimethylsulpholane supported on 30 - 60 mesh firebrick coupled to a 9m long, 6mm i.d. glass column (C) containing 5% S.E. 30 silicone oil supported on 30 - 60 mesh firebrick. This combination of columns was also found to be suitable for the separation of the products from the hydrogenation of buta-1,3-diene, so the later part of hydrogenation work was also carried out using this column. The operating conditions and the relevant retention data are shown in tables 3.1 and 3.2 for column A and (B + C) respectively.

Figure 3·2

The Gas Chromatography System

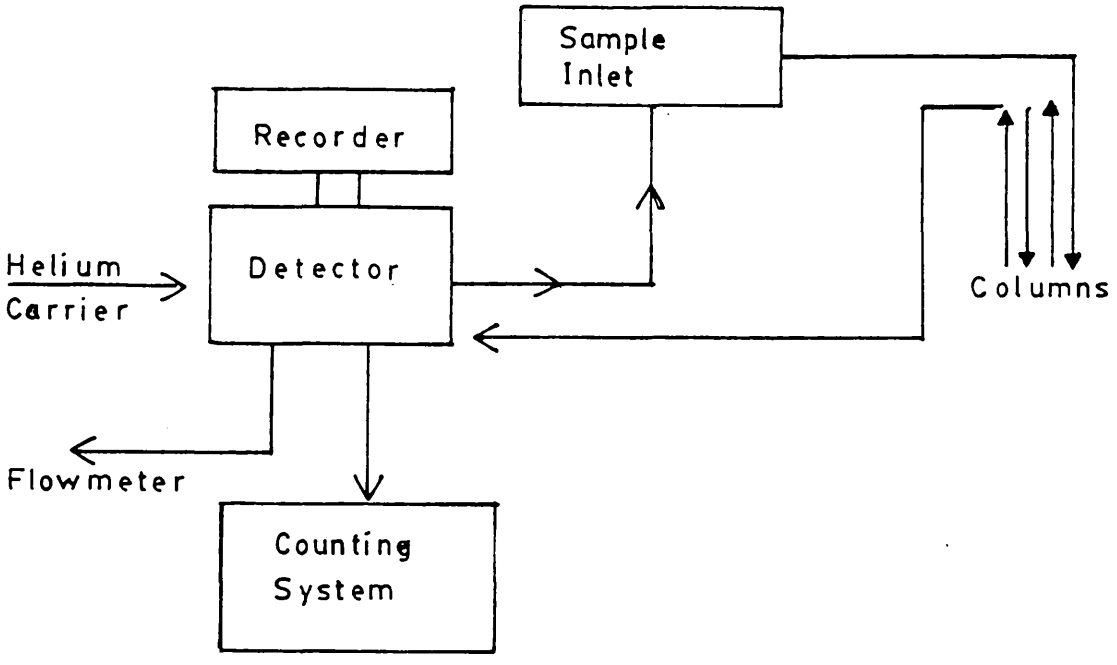


Figure 3·3

Sample Inlet System

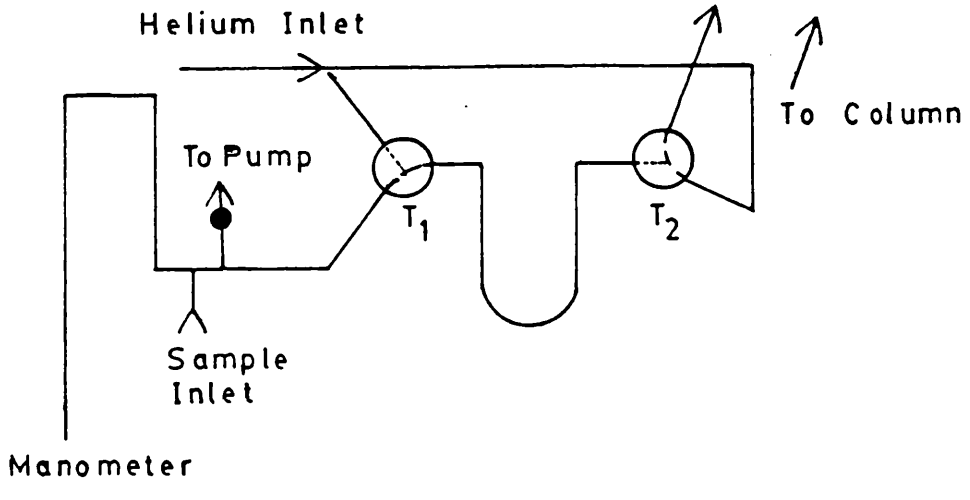


Table 3.1

Operating conditions and retention data for C_4-hydrocarbons on 33% dimethylsulpholane on firebrick (column A)

Temperature	20.0 ± 2°C
Carrier gas	Helium
Flow rate	35.0 ± 3ml/min
Inlet pressure	1.8 atmos. (approx.)
Hydrocarbon	Retention time (min)
n-Butane	17.50
But-1-ene	22.50
Trans-but-2-ene	26.25
Cis-but-2-ene	29.00
Buta-1,3-diene	37.50

Table 3.2

Operating conditions and retention data for 33% dimethylsulpholane/5% S.E. 30 silicone oil supported on firebrick (columns B and C)

Temperature	20.0 ± 2°C
Carrier gas	Helium
Flow rate	35 ± 3ml/min
Inlet pressure	1.8 atmos. (approx.)
Products	Retention time (min)
Propane	12.50
n-Butane	18.50
But-1-ene	22.50
Hydrogen sulphide	24.50
Trans-but-2-ene	26.50
Cis-but-2-ene	29.25
Buta-1,3-diene	38.00

Thiophene was permanently retained by each of the columns. Consequently, in the thiophene hydrodesulphurisation studies, no quantitative estimation of the amounts of thiophene in the reaction products could be made.

The detector was a Gow-Mac hot-wire katharometer, operated at a filament current of 200mA. The output from the detector was recorded on a Hitachi Perkin-Elmer Recorder 159 with a chart speed of 1cm/min. The flow rate of the helium

carrier gas, controlled by a Nupro precision needle valve, was measured by a bubble flowmeter connected to the outlet from the detector.

3.4.2 Procedure for the analysis

The sample vessel containing the reaction products was connected to the sample handling unit of the chromatograph via a B10 socket (figure 3.3). The system was evacuated, whilst the carrier gas was directed through the by-pass to the U-tube. The required pressure of products was introduced to the system, the pressure being measured by means of a mercury manometer. The taps T_1 and T_2 were turned simultaneously and the carrier gas was allowed to sweep the sample from the U-tube on to the column. A typical trace is shown in figure 3.4. Where very small samples were to be analysed or where it was desired to transfer the total products quantitatively, the whole sample was condensed into the U-tube by cooling it in liquid nitrogen then closing both the taps before allowing it to return to room temperature, after which the sample was introduced into the carrier gas stream.

In order to reduce errors due to day to day variations in experimental conditions, a sample of "standard" mixture of known composition and containing all the possible reaction products, was passed through the column before each series of analyses. The column was calibrated in terms of the ratio between the peak area and the corresponding partial pressure

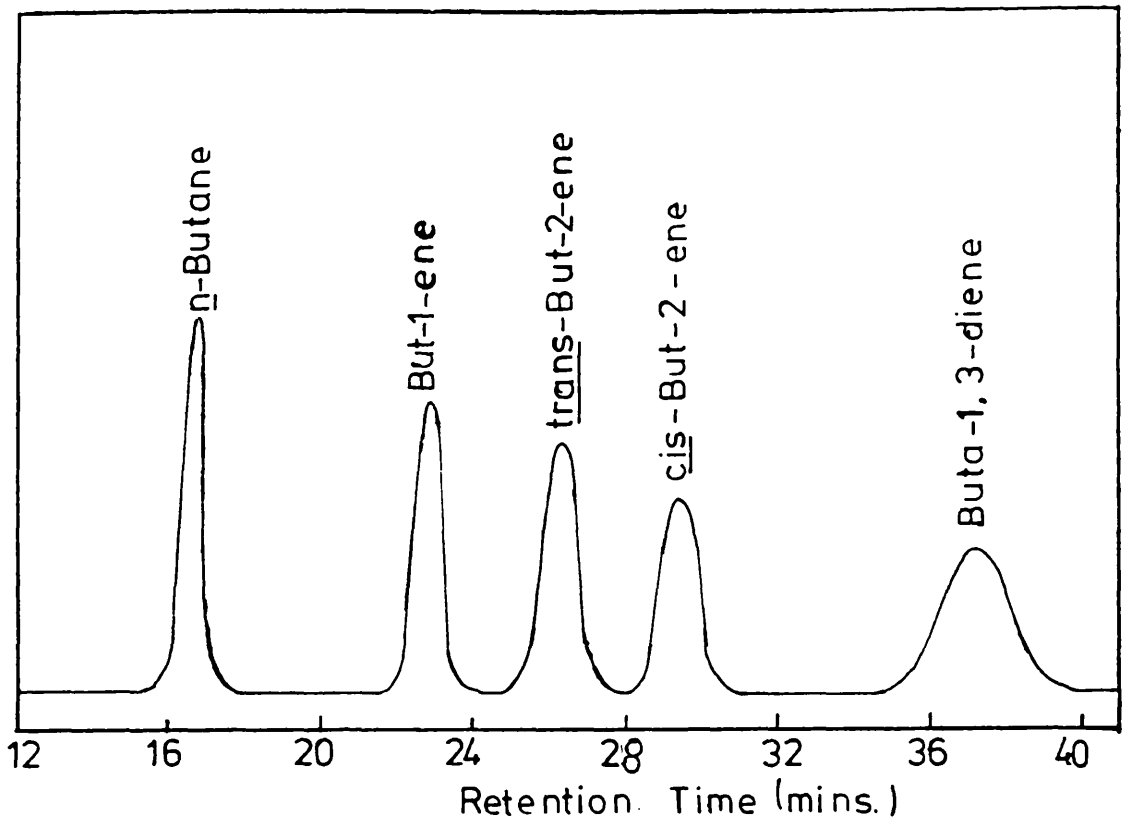


Figure 3.4(a) Separation of reaction products on the dimethylsulpholane column (column A)

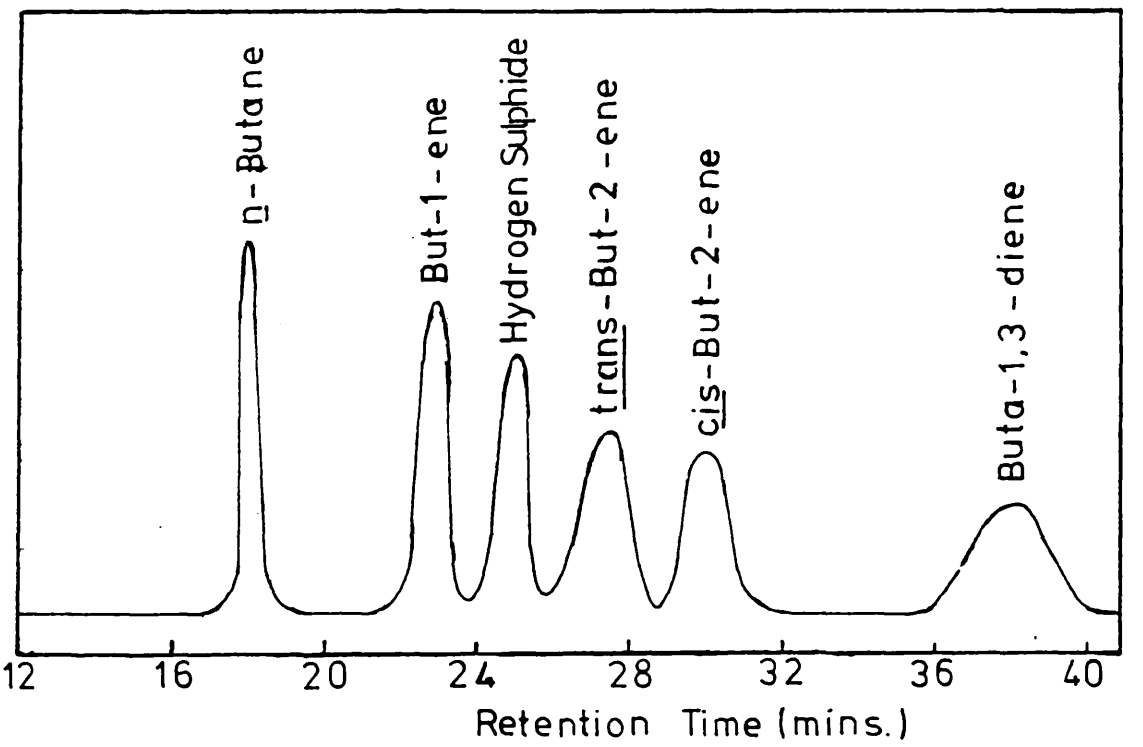


Figure 3.4(b) Separation of reaction products on the dimethylsulpholane - S.E.30 column (column B + C)

of each individual component, termed the "sensitivity coefficient". By measuring the area of each of the peaks in the chromatogram of an unknown reaction product mixture, it was thus possible to determine the partial pressure of each component in that mixture. The sensitivity coefficients for the relative hydrocarbons are shown in table 3.3.

Table 3.3

Operating conditions and the sensitivity coefficients for C_4-hydrocarbons for 33% dimethylsulpholane/5% S.E. 30 silicon oil supported on firebrick (columns B and C)

Temperature	20.0 ± 2°C
Carrier gas	Helium
Flow rate	35 ± 3ml/min
Inlet pressure	1.8 atmos. (approx.)
Hydrocarbons	**Sensitivity coefficient**
n-Butane	190.95
But-1-ene	185.71
Trans-but-2-ene	180.11
Cis-but-2-ene	180.00
Buta-1,3-diene	174.29
Hydrogen sulphide	36.73

3.5 Interaction of hydrogen sulphide with molybdenum disulphide catalysts

Part of the experimental work was concerned with determining the effects of hydrogen sulphide pretreatment upon the catalytic behaviour of the molybdenum disulphide. This necessitated an investigation of the interaction of hydrogen sulphide with the catalyst to determine (a) the extent of sulphur uptake, either as S^{2-} or HS^{-}, by the catalyst and (b) the extent of sulphur exchange between the gaseous hydrogen sulphide and the surface sulphur of the molybdenum disulphide catalyst.

Since the uptake of sulphur by the catalyst may lead to the formation of hydrogen, it was necessary to devise an experimental method whereby the accurate determination of the amounts of hydrogen sulphide adsorbed and of hydrogen produced could be made. The following method was used.

A known amount of hydrogen sulphide was allowed to expand from a standard volume ($5.907 cm^3$) containing a pressure (P_1) of hydrogen sulphide, into a larger volume comprised of the standard volume, reaction vessel containing the catalyst at $350^{o}C$, manometer and the associated dead spaces. The pressure (P_2) which it would then exert if it did not interact with the catalyst could be calculated from P_1 and the calibration constants of the apparatus (see section 3.6.1). After 30 minutes, the actual pressure (P_2') of the gas phase

was measured. The gas phase material in the reaction vessel was then pumped through a spiral trap cooled in liquid nitrogen, to remove any hydrogen, and the condensable material transferred quantitatively to the chromatograph where the yield of hydrogen sulphide, equivalent to a pressure P_3 in the reaction vessel, was determined. The amount of hydrogen could then be determined by difference.

[^{35}S]labelled hydrogen sulphide was used to determine the possible extent of sulphur exchange between the surface and gas phase. The experimental procedure was similar to that described above with the additional feature that, on elution from the chromatograph, the hydrogen sulphide was passed through the flow cell, described in section 3.7, and the total radioactivity and hence the specific activity (counts per torr) determined. The extent of exchange could thus be determined as the difference between the initial and final specific activities of the hydrogen sulphide.

3.6 Calibrations

3.6.1 Calibration of the apparatus

To carry out the procedure outlined in the previous section it was necessary to know the volumes of various sections of the apparatus.

The apparatus was equipped with a standard volume consisting of a closed vessel fitted with a stopcock. The

volume of this vessel was determined by weighing it, first empty and then filled with water, before it was attached to the apparatus, and the volume of the stopcock key was likewise determined using mercury. The volume of the vessel including that of the stopcock key was found to be 5.907cm^3.

In the catalysis studies, accurately known quantities of hydrogen sulphide were isolated in this standard vessel by filling it and the manometer and associated dead space with hydrogen sulphide at a pressure (P_1) which could be read on the manometer. The stopcock and the standard vessel were then closed to isolate the sample, and the manometer and dead space were evacuated.

For reasons already explained in section 3.5, it was necessary to know the ratio P_1/P_2 for the apparatus, where P_1 was the pressure in the standard vessel, and P_2 was the pressure of the same sample of gas after it had been allowed to expand into larger volume comprised of the standard vessel, reaction vessel at 350°C, the manometer and associated dead space. This was determined by calibration experiments performed with no catalyst in the reaction vessel. This procedure was repeated for several values of P_1 and the results are shown in table 3.4.

Table 3.4

Calibration of the reaction vessel for pressure measurements using hydrogen sulphide at 350°C

P_1(torr)	P_2(torr)	P_1/P_2
62.85	7.75	8.11
41.00	4.75	8.63
115.00	14.00	8.21
40.25	4.75	8.47
123.50	15.50	7.97
85.00	11.25	7.56
80.00	11.00	7.27

3.6.2 Calibration of the chromatography system

A known amount of hydrogen sulphide was taken in the standard vessel at room temperature, from where it was transferred to the empty reaction vessel at 350^{o}C. The sample was then condensed from the reaction vessel into a sample vessel for transfer to the gas chromatography system. The total sample was admitted to the chromatograph and the area of the corresponding chromatographic peak determined. The procedure was repeated for several different pressures of hydrogen sulphide in the standard volume and a calibration between these pressures and the corresponding chromatographic peak areas obtained as shown in figure 3.5.

In another series of calibration experiments, variable partial pressures of hydrogen sulphide and hydrogen were taken in the standard volume, expanded into the reaction vessel and then transferred to the gas chromatography system in order to simulate the conditions of an actual catalysis experiment. Figure 3.6 shows that the peak area of hydrogen sulphide was proportional to its partial pressure in the mixture.

3.7 The Radiochemical system

In order to determine quantitatively the amounts of [^{35}S]-hydrogen sulphide in the hydrogen sulphide eluted from the chromatograph, a flow cell (figure 3.7), incorporating a Mullard MX 168/01 end window G.-M. counter, was attached to

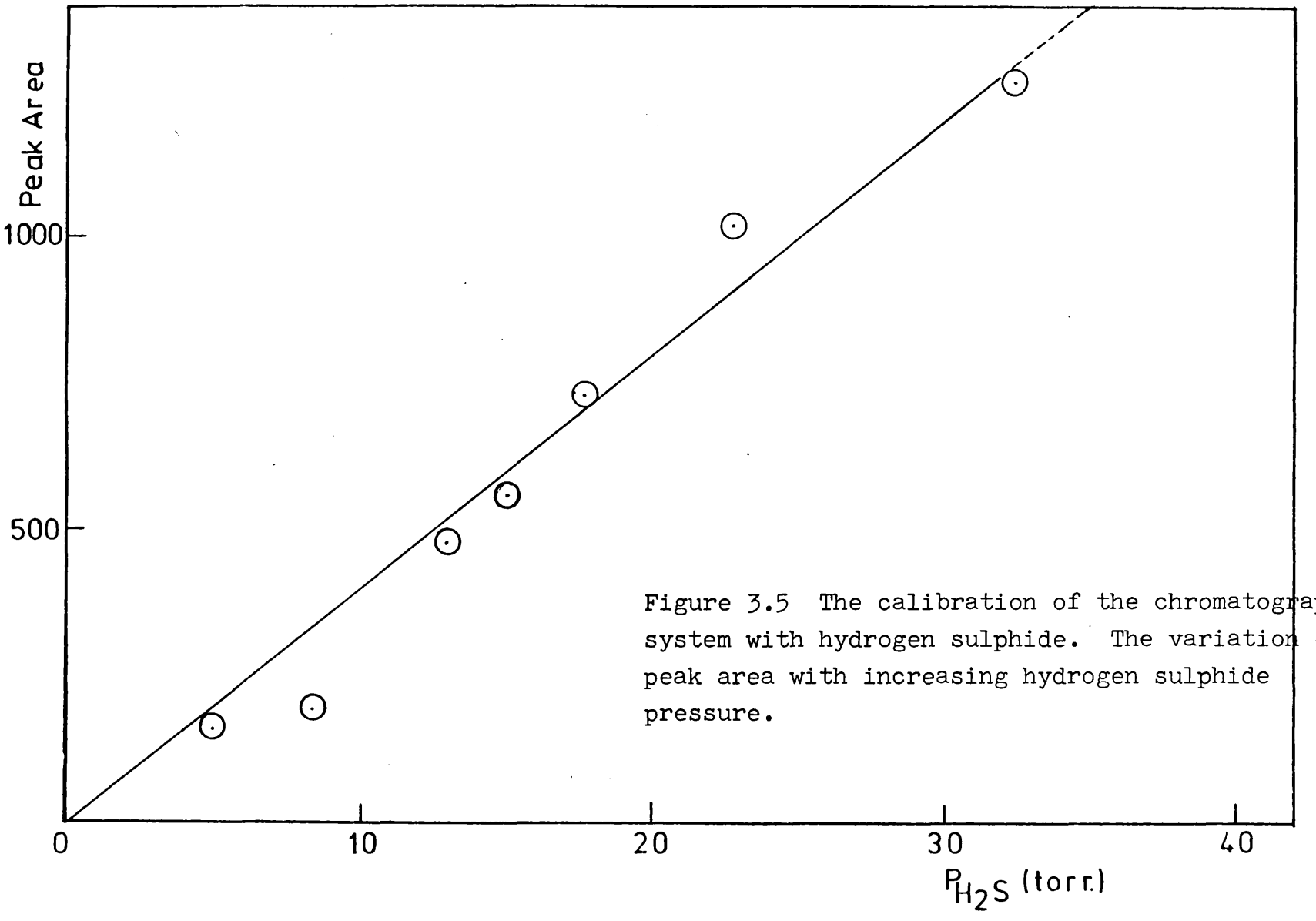


Figure 3.5 The calibration of the chromatography system with hydrogen sulphide. The variation of peak area with increasing hydrogen sulphide pressure.

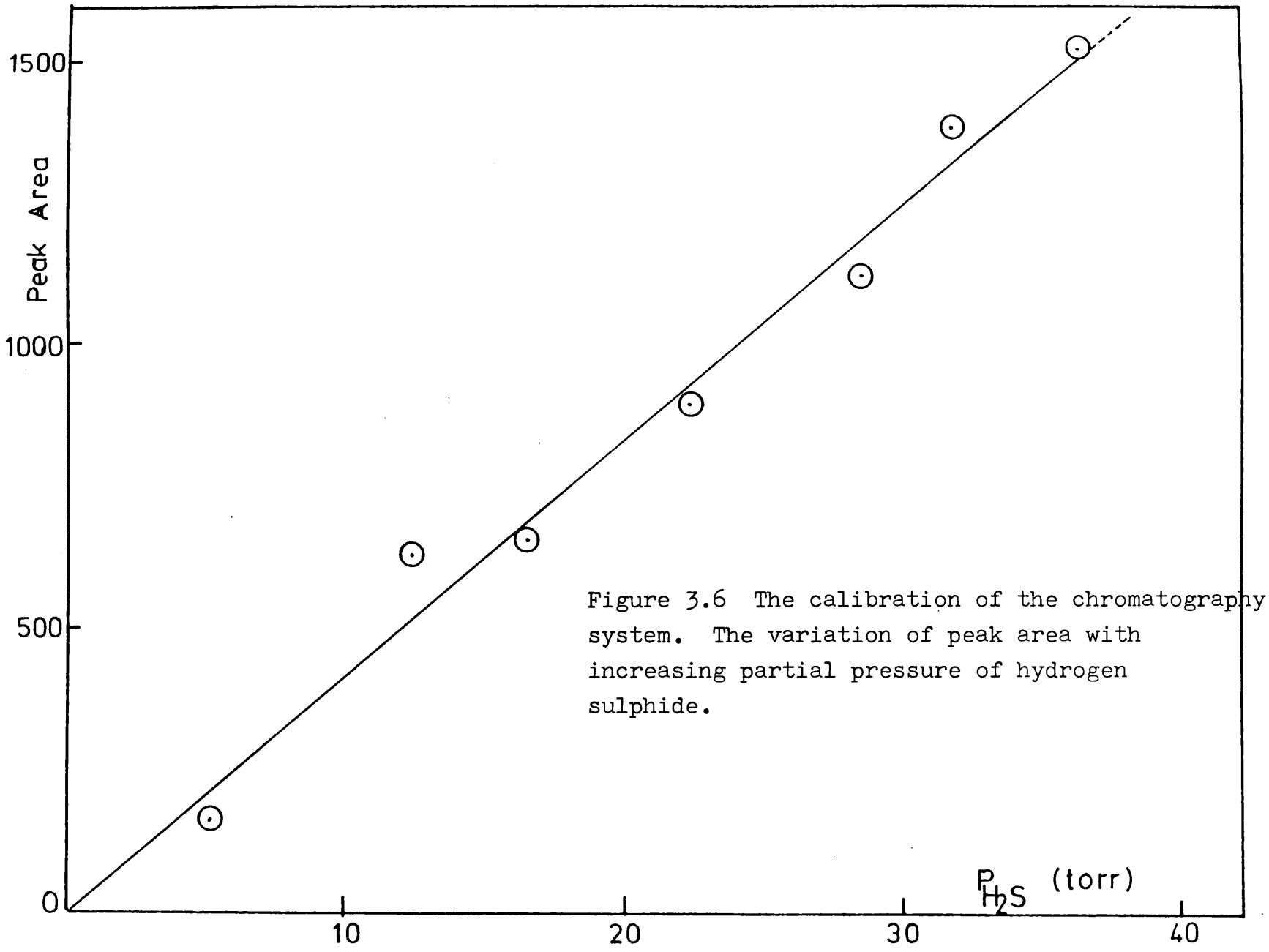
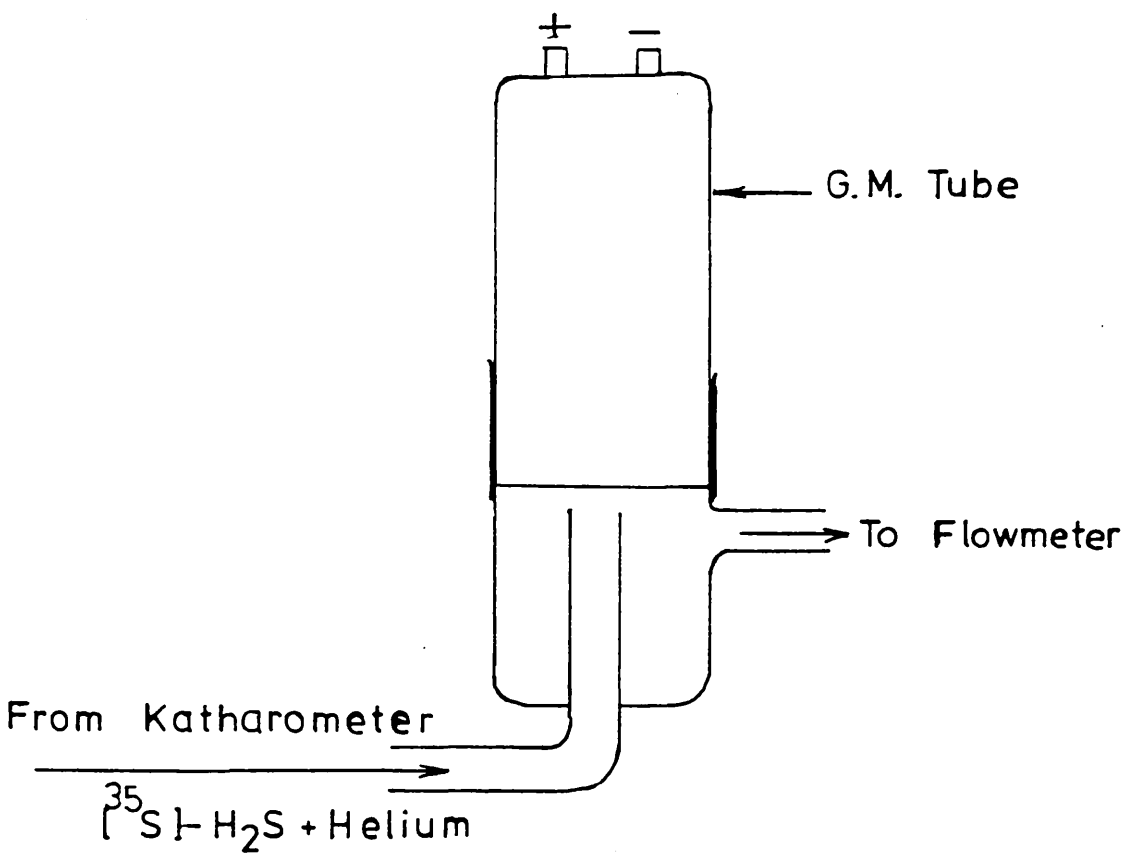


Figure 3.6 The calibration of the chromatography system. The variation of peak area with increasing partial pressure of hydrogen sulphide.

Figure 3·7

The Flow Cell



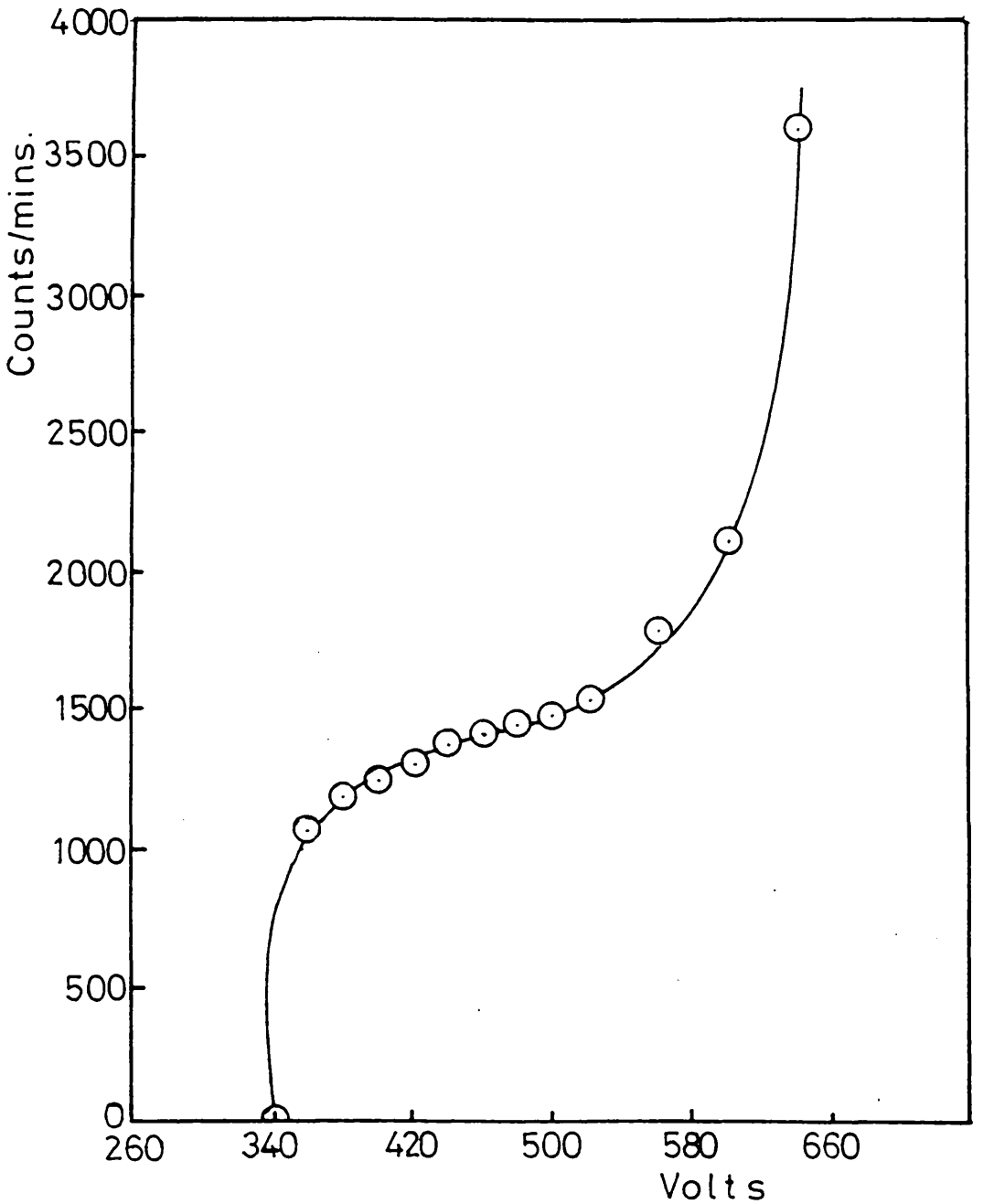
the outlet of the chromatographic system. The detector was connected to an Autoscaler-Timer Frequency Ratemeter (Isotope Developments Ltd.), the output from which was fed directly to a potentiometric chart recorder.

The plateau region of the G.-M. counter was determined using an external [^{137}Cs]source as shown in figure 3.8. The quantitative behaviour of the counter was tested by passing different amounts of [^{35}S]-hydrogen sulphide through the flow cell under standard flow conditions. A linear relationship between the total number of counts and the amount of [^{35}S]-hydrogen sulphide admitted was obtained.

The efficiency of the counter was dependent upon day to day experimental conditions, owing to small variations in temperature, flow rate of the carrier gas and also due to the deposition of radioactive material on the window. The specific activity of [^{35}S]-hydrogen sulphide decreased during usage owing to decay, since the half life of [^{35}S]-hydrogen sulphide is only 87 days. A calibration check was carried out at regular intervals to allow for any change in either the counter efficiency or the specific activity of the starting material.

Figure 3·8

G.M. Tube Plateau



CHAPTER 4

4. TREATMENT OF RESULTS

4.1 The measurement of initial rates of reactions

Initial rates of reactions were calculated from pressure fall against time curves; the gradient of the tangent to the curve at zero time, or the gradient of the line itself if it was linear, was measured and taken to represent the initial rate of reaction.

4.2 Determination of activation energy

Initial rates were measured as a function of temperature in a series of reactions where the same reactant pressure ratio was used. The activation energies were then determined from the Arrhenius equation

$$k = A \exp. (-E_a/RT)$$

by plotting log k against $\frac{1}{T}$.

4.3 Determination of reaction kinetics

The dependence of reaction rates upon the initial pressure of the reactant was calculated on the assumption that the rate expression is of the form

$$r = kP_A^{x}P_B^{y}$$

where r = rate of reaction

k = rate constant

P_A = initial pressure of reactant A

P_B = initial pressure of reactant B

x,y = order of reaction with respect to A and B respectively.

To determine the order of reaction with respect to one of the reactants, the initial pressure of that reactant was varied, whilst the initial pressure of the other reactant was kept constant in a series of reactions at a constant temperature. Orders of unity and zero could be instantly recognised from plots of initial rate against the initial pressure of the reactant. Non-integral orders were determined from the slopes of the plots of $\log_{10}$ (rate) against $\log_{10}$ (initial pressure).

4.4 Interpretation of chromatography traces

By calibration with varying amounts of known composition, the area under a peak in the chromatography traces was found to be proportional to the quantity of the component which it represented, the ratio (peak area/quantity), being termed the sensitivity coefficient. For reaction mixtures, the senistivity coefficient was used to calculate the quantities and hence the percentage distribution of the products. The distribution of each butene was also expressed as a percentage of the total butene pressure.

CHAPTER 5

5. The Reaction of Buta-1,3-Diene with Hydrogen on Molybdenum Disulphide Catalysts

5.1 Introduction

This chapter is concerned with the reaction of buta-1,3-diene over samples of molybdenum disulphide catalyst. The dominant feature to emerge from the product analysis was that in the early stages of the reactions the selectivity was almost unity. The formation of n-butane commenced only after most of the buta-1,3-diene had been converted to butenes. The selectivity, S, is defined as;

$$S = \frac{\text{yield of butene}}{\text{yield of butene + n-butane}}$$

The terms buta-1,3-diene, but-1-ene, trans-but-2-ene, cis-but-2-ene, propane and thiophene are abbreviated to 1-3B, 1-B, t-2-B, c-2-B, Pr and T.P. respectively. The term butadiene will be used to refer to buta-1,3-diene, since buta-1,2-diene has not been used in this work.

5.2 The pressure against time curves

Figure 5.1 shows the pressure fall against time curve for the reaction of butadiene at 350^{o}C, using an initial butadiene pressure of 50 torr and an initial hydrogen pressure of 100torr. The pressure against time curve showed a

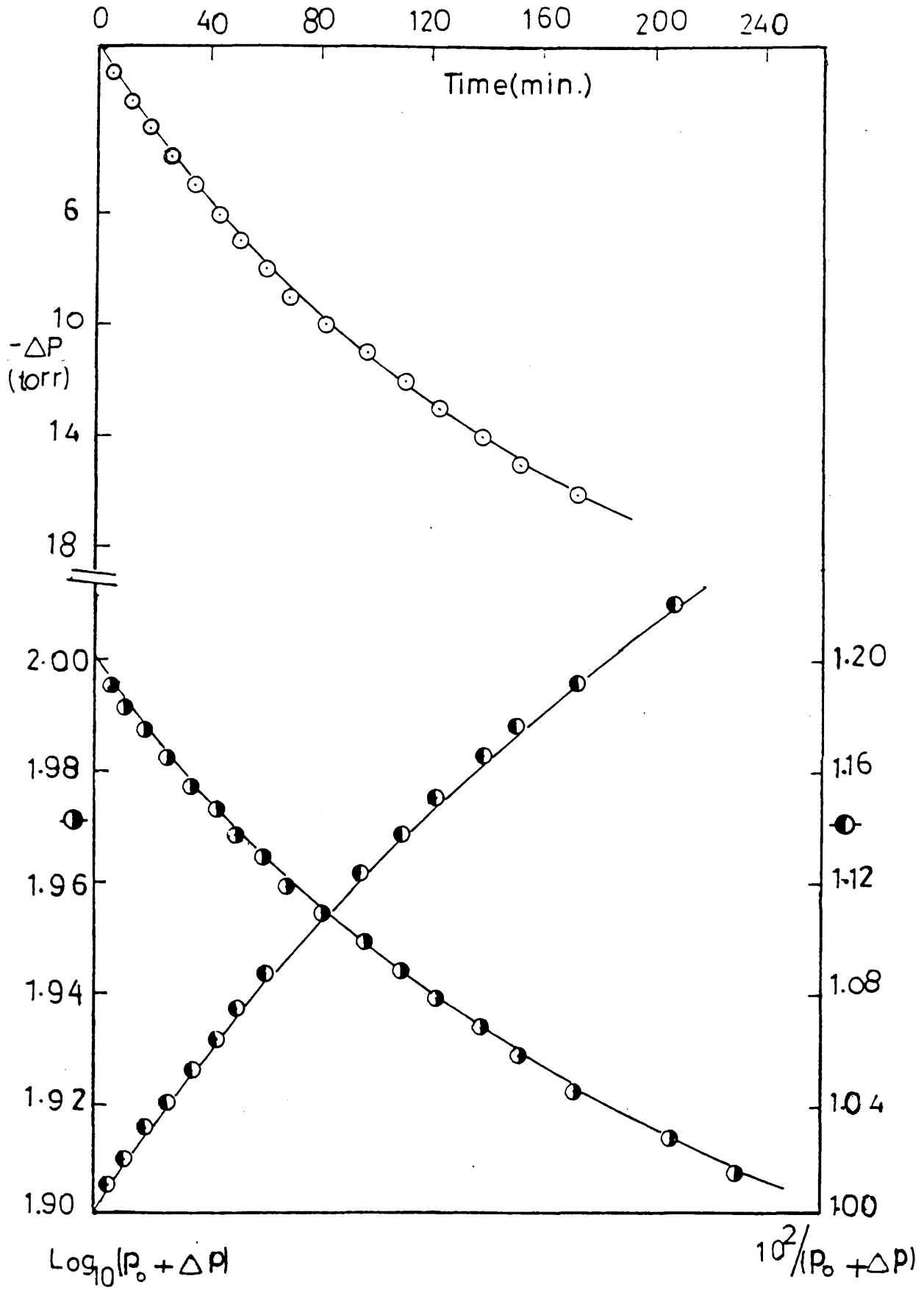


Figure 5.1 A typical pressure fall against time curve for the reaction of 50 torr of butadiene with 100 torr of hydrogen at 350°C over fresh molybdenum disulphide. Also shown are the plots to test for first and second order.

continuous decrease in rate. Also shown in figure 5.1 are function plots to test for first and second order reactions. It can be seen that the reaction showed an order intermediate between first and second.

5.3 The variation of reaction rate and butene distribution with reaction number

A series of reactions was carried out at 350 ± 2°C over 0.50g of catalyst, to investigate whether the rate and the butene distribution changed with increasing use of the catalyst over several runs. The pressure fall versus time curves (figure 5.2) show that the rate became fairly constant after the second run.

In another series of reactions at 350 ± 2°C, using a catalyst weighing 0.576g with a hydrogen:butadiene ratio of 3:1, the products were extracted for analysis after a fixed pressure fall of 10.0 ± 0.5torr. The distribution of butenes from this series of reactions is shown in table 5.1 and figure 5.3, which shows that at first the butene distribution varied from one reaction to another, but the variation in the product distribution became negligible after two or three runs.

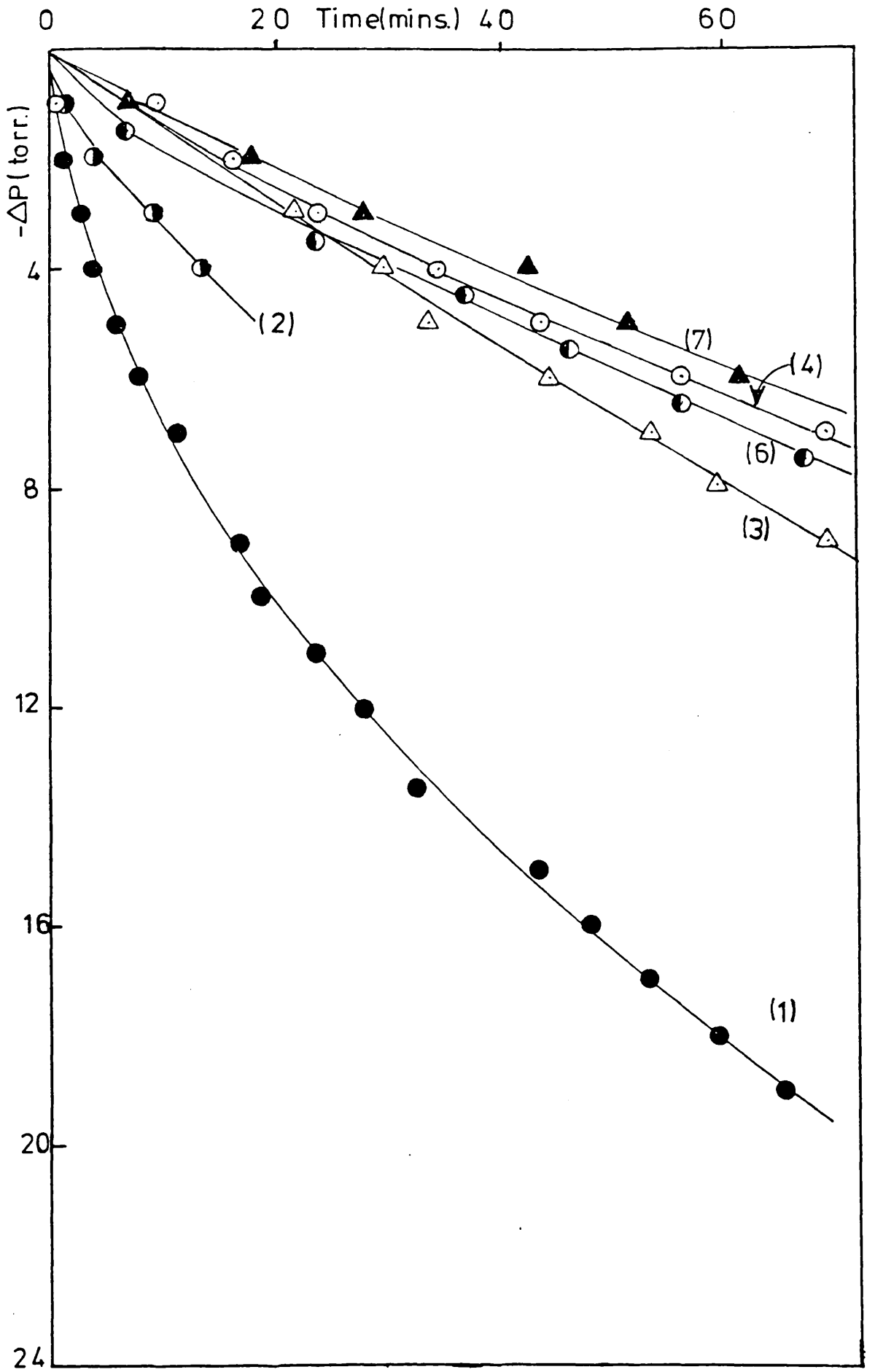


Figure 5.2 Series of pressure fall against time curves for hydrogenation of butadiene at 350°C using butadiene:hydrogen ratio 1:3

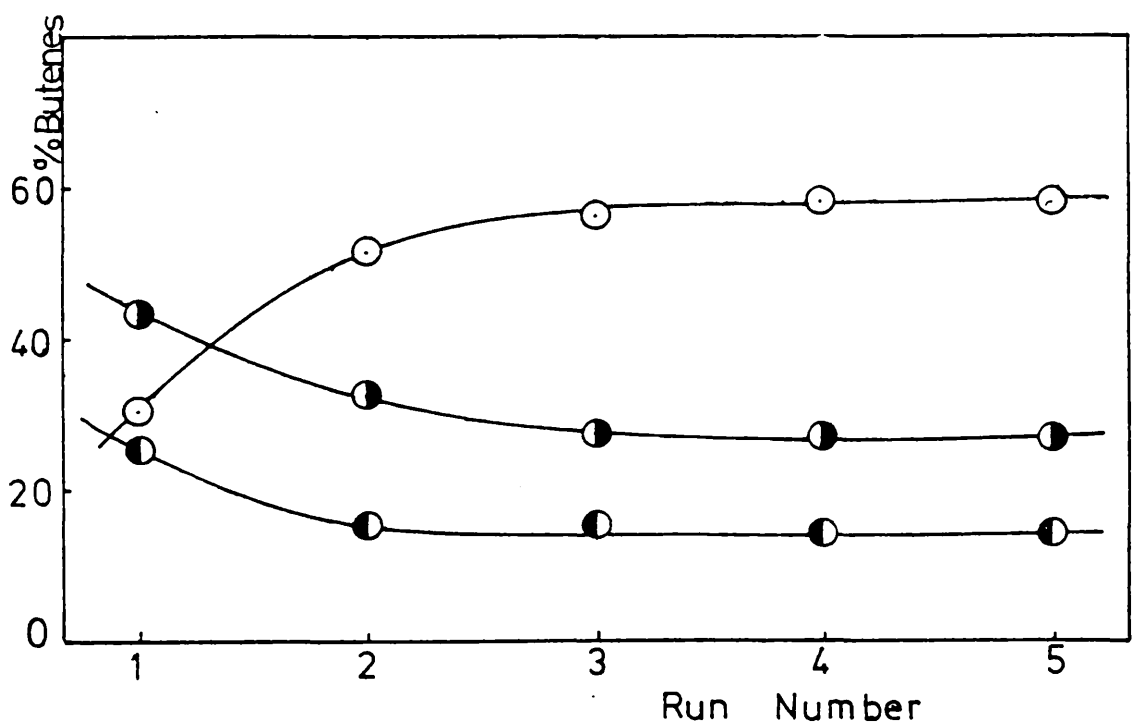
Table 5.1

Variation of initial rate and butene distribution with reaction number

Temperature = 350.0 ± 2.0°C; initial butadiene pressure = 50.0 ± 0.5torr; initial hydrogen pressure 150.0 ± 1.0torr; pressure fall at extraction = 10.0 ± 0.5torr.

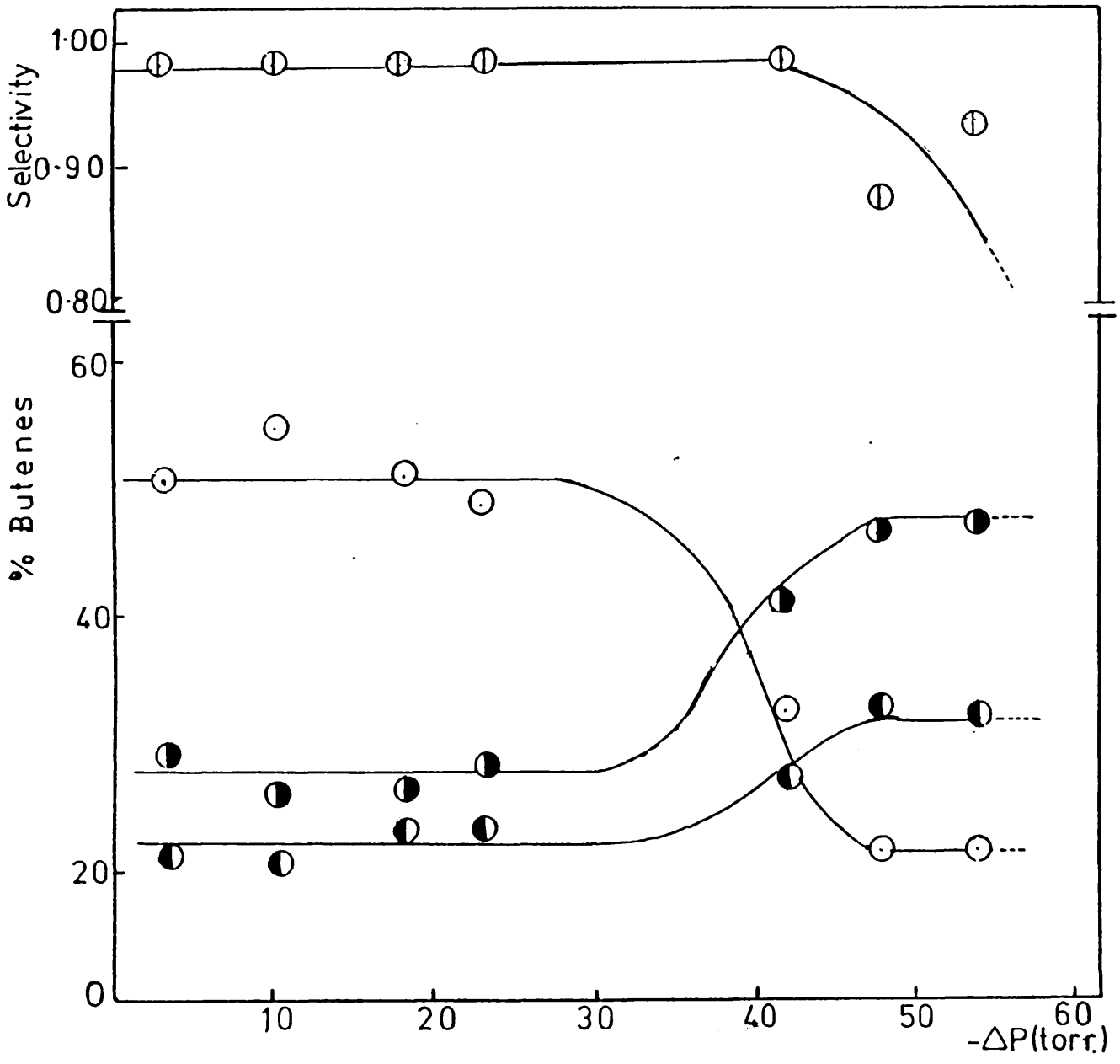
Reaction	Butene distribution			$(\frac{trans}{cis})$	Initial rate
	1-B	t-2-B	c-2-B		(torr/min.)
$^{A}/_{1}$	30.3	43.9	25.8	1.70	1.50
$^{A}/_{2}$	51.7	32.7	15.6	2.10	2.40
$^{A}/_{3}$	56.4	27.8	15.8	1.76	1.50
$^{A}/_{4}$	58.3	27.6	14.1	1.96	1.43
$^{A}/_{5}$	58.7	27.0	14.3	1.89	1.11

Figure 5.3 The variation of butene distribution with reaction number over fresh molybdenum disulphide at 350°C.



5.4 The variation of selectivity and butene distribution with conversion

In a series of reactions at 350°C, over a sample of fresh catalyst (0.402g) using a hydrogen:butadiene ratio of 3:1, five consecutive reactions were carried out and the products were extracted at a constant pressure fall of 10.0 ± 0.5torr. This was done to minimise any effect of reaction number on butene distribution, that is, to 'run in' the catalyst to a state of reproducible performance. A series of butadiene hydrogenation reactions was then carried out over the same catalyst and the products were extracted at varying pressure falls. The reactions were carried out in a random order. In the early stages of the reactions the butene distribution was independent of conversion as shown in figure 5.4, the selectivity was almost unity, and the formation of n-butane commenced only after most of the butadiene had been converted to butenes. The variation of selectivity and butene distribution with varying pressure fall is shown in table 5.2.



But-1-ene

trans-But-2-ene

cis-But-2-ene

Selectivity

Figure 5.4 The variation of butene distribution with increasing extent of reaction over fresh molybdenum disulphide at 350°C.

Table 5.2

The variation of selectivity and butene distribution with conversion

Reaction	-ΔP(torr)	Butene distribution				Selectivity
		1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	
$^{B}/_{4}$	3.25	50.3	28.6	21.1	1.36	0.983
$^{B}/_{1}$	10.0	54.4	25.2	20.4	1.24	0.980
$^{B}/_{2}$	18.0	50.7	26.0	23.3	1.12	0.980
$^{B}/_{6}$	23.0	48.2	28.2	23.6	1.19	0.982
$^{B}/_{3}$	42.0	32.4	40.6	27.0	1.50	0.982
$^{B}/_{5}$	48.0	21.6	46.3	32.1	1.44	0.874
$^{B}/_{7}$	54.0	21.5	46.9	31.6	1.48	0.937

5.5 The order with respect to hydrogen and the dependence of butene distribution upon initial hydrogen pressure

In a series of experiments at 358^{o}C, using a constant initial butadiene pressure of 50.0torr, the hydrogen pressure was varied between 50.0 and 280.0torr. The products were extracted for analysis after a pressure fall of 5.0torr. The butene composition was found to be independent of the initial hydrogen pressure. The results are shown in table 5.3. The order with respect to hydrogen was found to be unity as shown in figure 5.5.

Table 5.3

The variation of initial rate and butene distribution with initial hydrogen pressure

Temperature = 358°C; initial butadiene pressure = 50.0 ± 0.5torr; pressure fall at extraction = 5.0torr.

Reaction	P_{H_2} (torr)	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	Initial rate (torr/min.)
$C_{/2}$	50.0	56.9	25.5	17.6	1.45	0.39
$C_{/5}$	75.0	53.4	28.1	18.5	1.52	0.50
$C_{/4}$	100.0	55.5	26.9	17.6	1.53	0.75
$C_{/3}$	200.0	54.9	28.1	17.0	1.65	2.28
$C_{/1}$	280.0	57.4	26.9	15.7	1.71	2.00

A prolonged reaction was carried out at 350°C, using an initial butadiene pressure of 49torr and an initial hydrogen pressure of 341torr. The products were extracted after a pressure fall of 23.0torr. The product analysis showed that n-butane was the major product. The reaction analysis was n-butane = 90.8%; but-1-ene = 1.2%; trans-but-2-ene = 4.7%; cis-but-2-ene = 3.3%.

5.6 The order with respect to butadiene

In a series of reactions at 360°C, the initial butadiene pressure was varied between 25.0 and 200.0torr at a constant hydrogen pressure of 150.0torr. The results presented in table 5.4 show that the butene distribution was independent of the initial butadiene pressure. Figure 5.6 shows a plot of initial rate against initial butadiene pressure. It can be seen that the initial order with respect to butadiene is unity.

Table 5.4

The variation of initial rate and the distribution of butenes with increasing butadiene pressure

Temperature = 360.0 ± 2.0torr; initial hydrogen pressure = 100.0 ± 1.0torr; weight of the catalyst = 0.402g.

Reaction	P_{1-3B} (torr)	$-\Delta P_{ext.}$ (torr)	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	Initial rate (torr/min.)
$D/2$	25.0	2.5	51.9	29.3	18.8	1.56	0.20
$D/4$	75.0	7.0	57.3	26.3	16.4	1.60	0.50
$D/1$	100.0	10.0	58.5	25.9	15.6	1.66	1.14
$D/3$	200.0	20.0	55.9	27.7	16.4	1.69	1.60

5.7 Temperature dependence of the butene distribution and the activation energy

In a series of reactions in the temperature range 314°C to 424°C, using a hydrogen:butadiene ratio 3:1 and the variation of initial rate was studied as a function of temperature. All the reactions were analysed after a pressure fall of 5.0torr. The results are shown in table 5.5. The plot of $\log_{10}$ (initial rate) against the reciprocal of absolute temperature (figure 5.7) produced a straight line from which an activation energy of 48.5 ± 3.0 kJ/mole was obtained.

Table 5.5

The variation of initial rate and butene distribution with increasing temperature

Initial butadiene pressure = 50.0 ± 0.5torr; initial hydrogen pressure = 150.0 ± 1.0torr; pressure fall at extraction = 5.0torr.

Reaction	Temp. °C	$-\Delta P_{ext}$ (torr)	Butene distribution			$(\frac{trans}{cis})$	1-B / 2-B	Initial rate (torr/min)
			1-B	t-2-B	c-2-B			
$E_{/4}$	314	5.0	48.4	30.4	21.2	1.43	0.94	0.37
$E_{/2}$	341	5.0	55.5	26.9	17.6	1.53	1.25	0.61
$E_{/5}$	355	-	-	-	-	-	-	1.00
$E_{/3}$	391	5.0	54.1	26.8	19.1	1.40	1.18	1.25
$E_{/1}$	424	5.0	55.9	26.0	18.1	1.44	1.27	1.60

Reaction $E_{/5}$ was not analysed.

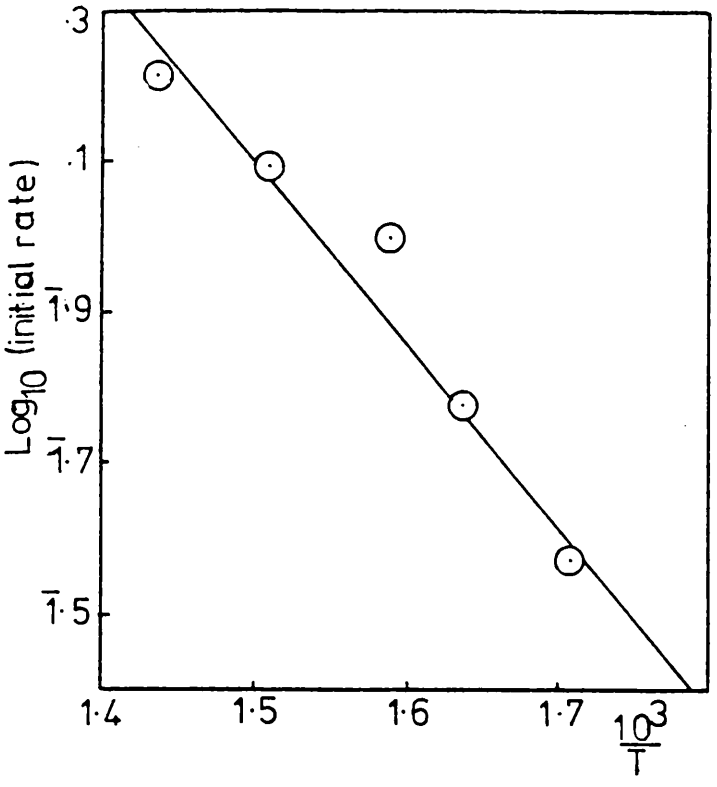


Figure 5.7 The variation of $\log_{10}$ (initial rate) with the reciprocal of the absolute temperature over fresh molybdenum disulphide.

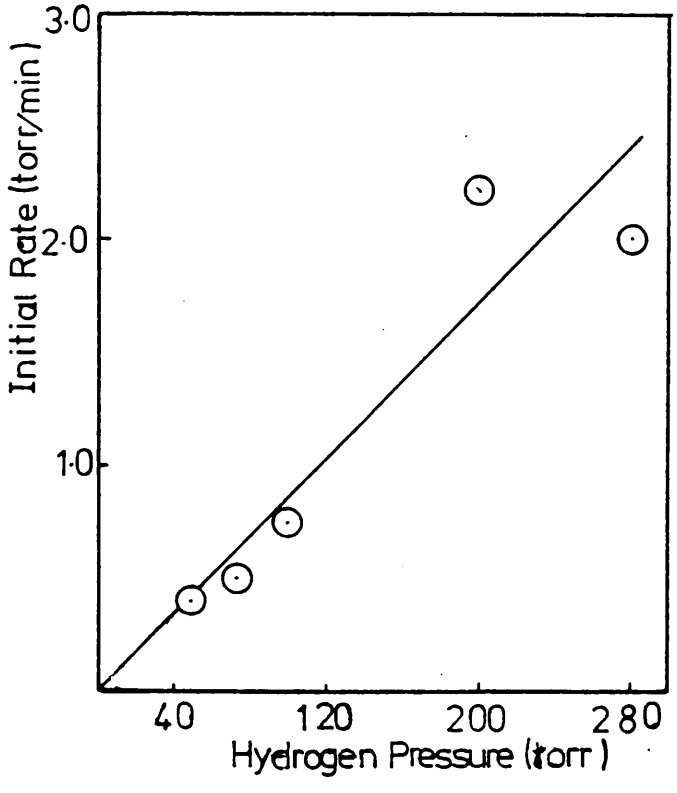


Figure 5.5 The variation of initial rate with increasing hydrogen pressure at 358°C.

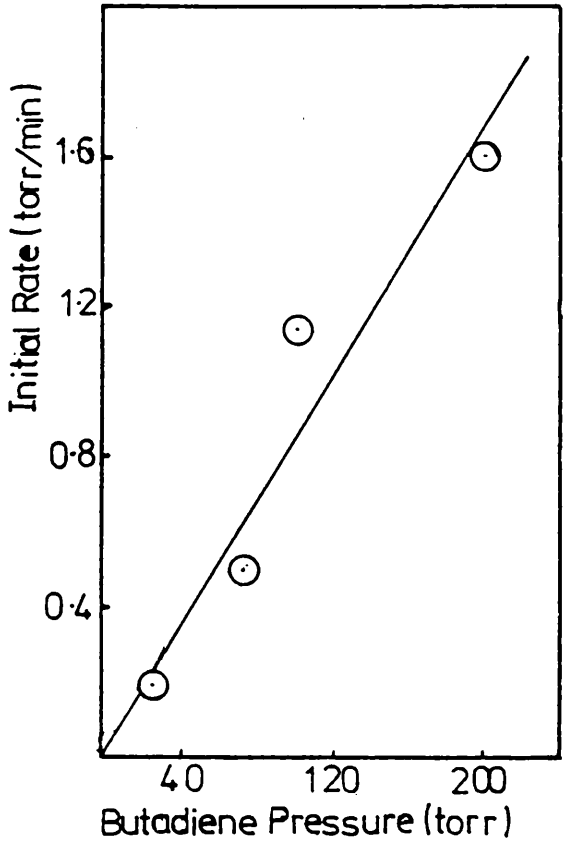


Figure 5.6 The variation of initial rate with increasing butadiene pressure at 360°C.

5.8 The effect of pretreatment of the catalyst on the initial rate of reaction and the butene distribution

Three series of reactions (F, G and H) were carried out, each on a separate sample of fresh catalyst which had been pretreated in different ways. The reactions were carried out at 350°C, using a hydrogen:butadiene ratio of 3:1 and the products were extracted at a fixed pressure fall of 10.0 ± 0.5torr.

Series F

A fresh catalyst (0.576g) was heated *in vacuo* up to 350°C. The catalyst was then treated with two changes of hydrogen (~300torr) at 350°C for a total of four hours. In a series of five butadiene hydrogenation reactions over the hydrogen treated catalyst at 350°C, the products were extracted at a pressure fall of 10.0torr. The results are given in table 5.6. The distribution of butene varied from one reaction to another; the percentage yield of but-1-ene increased relative to the but-2-ene yield, (figure 5.8). There was, however, no significant change in $\frac{\text{trans}}{\text{cis}}$ ratio from one run to another. The initial rate of reaction over the hydrogen treated catalyst was higher than that observed with the catalysts studied in series G and H (figure 5.9), described below.

Table 5.6

The variation of initial rate and the butene distribution over a hydrogen treated molybdenum disulphide catalyst (series F)

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
$F_{/1}$	58.1	25.6	16.3	1.57	1.39	8.00
$F_{/2}$	64.5	21.8	13.7	1.59	1.82	7.00
$F_{/3}$	63.4	22.1	14.5	1.52	1.73	4.00
$F_{/4}$	64.4	21.4	14.2	1.51	1.81	3.00
$F_{/5}$	-	-	-	-	-	2.5

Reaction $F_{/5}$ was not analysed.

Series G

Another sample of catalyst weighing 0.57g was evacuated for one hour, heated gradually up to 350°C in vacuo and then kept at 350°C under vacuum with continuous pumping for about an hour. A series of five butadiene hydrogenation reactions was carried out at 350°C. The products were extracted after a pressure fall of 10.0torr and analysed. The butene distribution varied from one reaction to another. The significant changes were in the first two runs. In subsequent runs, the butene distribution was virtually independent of run number (figure 5.8). The initial rate of reaction was low compared to the catalyst treated with

hydrogen. Table 5.7 shows the butene distribution and the initial rate as a function of run number.

Table 5.7

The variation of initial rate and the butene distribution with reaction number over the fresh 'evacuated' catalyst (series G)

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate
	1-B	t-2-B	c-2-B			(torr/min.)
G/1	30.3	43.9	25.8	1.70	0.43	1.50
G/2	51.7	32.7	15.6	2.10	1.07	3.00
G/3	56.4	27.8	15.8	1.76	1.29	1.50
G/4	58.3	27.6	14.1	1.96	1.40	1.50

Series H

A third series of reactions was carried out over another sample of catalyst (0.57g). This sample of catalyst was treated with hydrogen (400torr) for six hours at 350°C, evacuated at the same temperature for 30 minutes, then exposed to air (~45torr) at 350°C for two hours. The variation of butene distribution and the initial rate of reaction were compared with the catalyst pretreated with hydrogen. A series

of five butadiene hydrogenation reactions was carried out over this catalyst at 350°C. The products were analysed at a pressure fall of 10.0torr. The trend in the butene distribution was similar to that observed with the hydrogen pretreated catalyst (series F and H), as can be seen in figure 5.8. The initial rate of reaction was low compared with the catalyst pretreated with hydrogen but it was higher than that obtained with the fresh evacuated catalyst. The results are shown in table 5.8.

The variation of initial rate of reaction with the reaction number over the catalysts in series F, G and H is shown in figure 5.9.

Table 5.8

The variation of initial rate and the butene distribution with reaction number over air treated catalyst (series H)

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate
	1-B	t-2-B	c-2-B			(torr/min.)
H/1	48.3	27.4	24.3	1.13	0.93	5.00
H/2	54.4	24.5	21.1	1.16	1.19	3.25
H/3	60.6	21.8	17.6	1.24	1.54	3.00
H/4	55.7	24.1	20.2	1.19	1.26	2.00
H/5	54.0	25.4	20.6	1.23	1.17	2.00

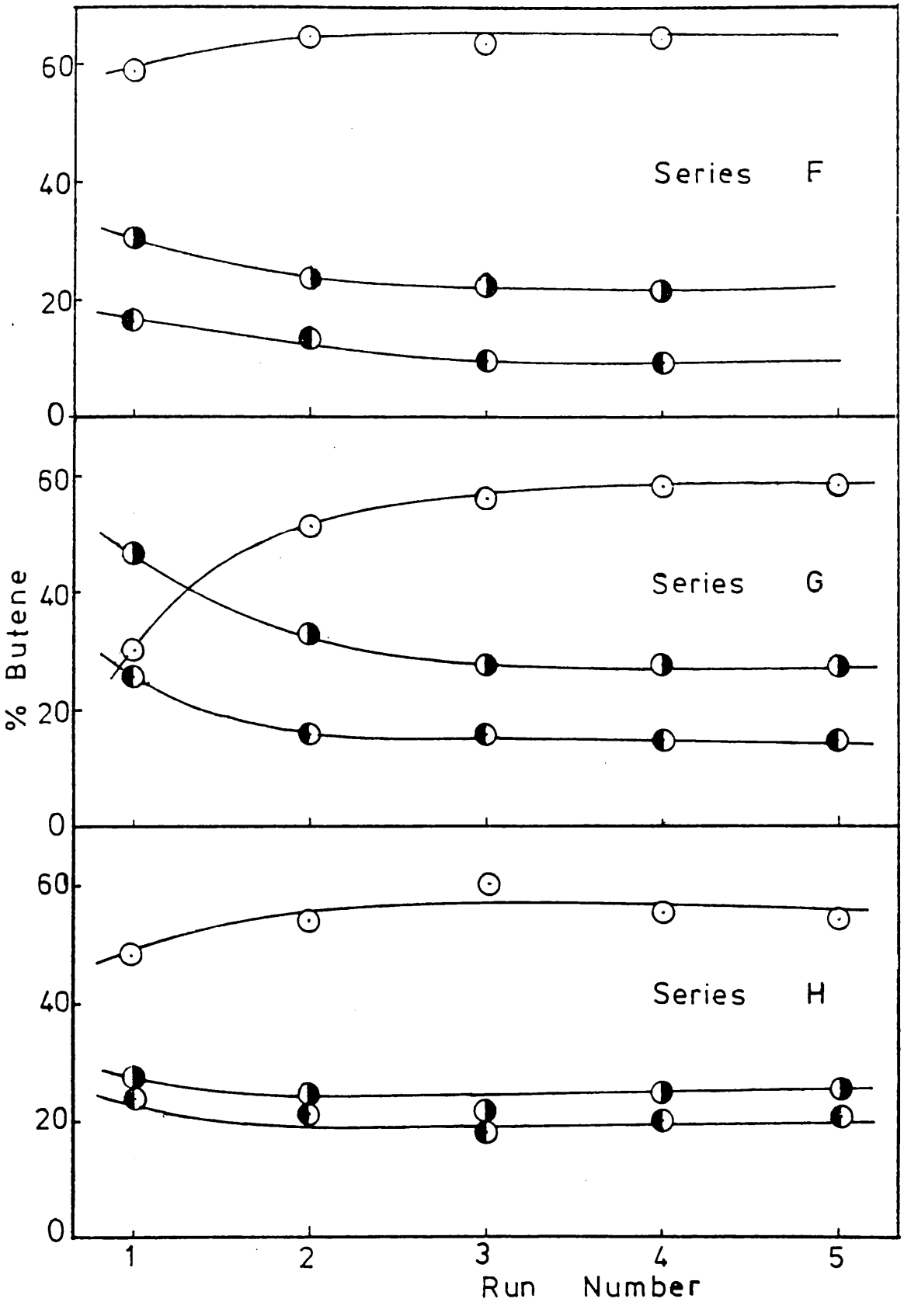


Figure 5.8 The variation of butene distribution with reaction number over various pretreated molybdenum disulphide catalysts at 350°C (⊙, 1-B ; ◑, t-2-B; ◐, c-2-B).

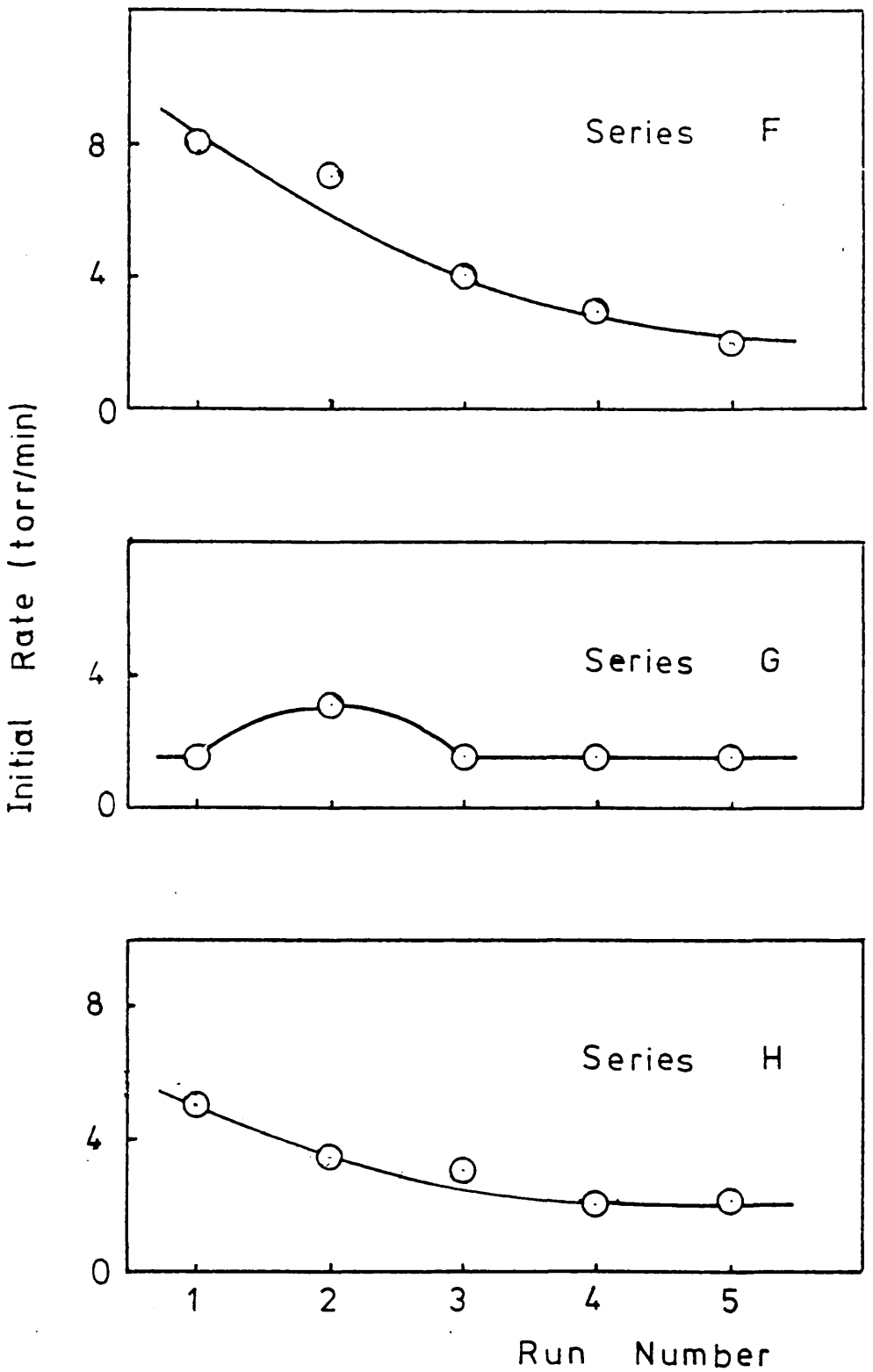


Figure 5.9 The variation of initial rate with reaction number over various pretreated molybdenum disulphide catalysts at 350°C.

5.9 The effect of air upon the activity and selectivity of the catalyst

A catalyst (0.402g) which had previously been used for several butadiene hydrogenation reactions was used to investigate the possible influence of oxygen contamination upon the activity and selectivity of the catalyst. Three butadiene hydrogenation reactions (series I) were carried out at 350°C using a hydrogen:butadiene ratio of 3:1. In this and the subsequent series of reactions, described in this section, the products were extracted at a fixed pressure fall of 10.0torr. The results are given in table 5.9. The catalyst was then exposed to air (~200torr) at 350°C for 20 minutes, evacuated, and three more butadiene hydrogenation reactions (series J) were carried out under the same experimental conditions. No n-butane was observed as a reaction product. There was no marked change in the butene distribution obtained with this catalyst, before and after exposing it to air. Subsequent re-exposure of the catalyst to air (1 atm.) at 350°C for 16 hours, followed by butadiene hydrogenation reactions (series K) again did not produce changes in butene distribution. A significant influence of the exposure to air was found, however, in the initial rate of reaction. On exposure to air, the catalyst exhibited higher activity as compared with that observed before exposure of the catalyst to air. The results are shown in table 5.9 and figure 5.10.

Table 5.9

Temperature = 350°C; initial butadiene pressure = 50.0 ± 0.5torr; initial hydrogen pressure = 150.0 ± 1.0torr; pressure fall at extraction = 10.0 ± 0.5torr.

The variation of initial rate and butene distribution over the used catalyst

Reaction	Butene distribution			$(\frac{trans}{cis})$	Initial rate
	1-B	t-2-B	c-2-B		(torr/min.)
$^{I}/1$	46.0	39.6	14.4	2.75	0.90
$^{I}/2$	42.8	34.9	22.3	1.57	0.80
$^{I}/3$	41.4	36.5	22.1	1.65	0.80

The variation of initial rate, and butene distribution over air treated catalyst

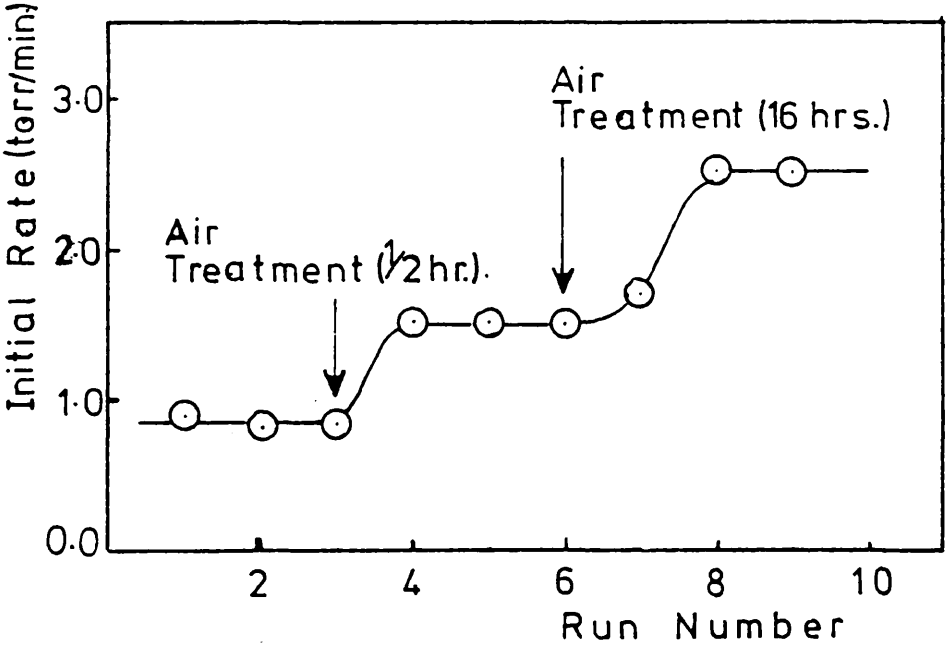
Time of exposure to air = 30 minutes

Reaction	Butene distribution			$(\frac{trans}{cis})$	Initial rate
	1-B	t-2-B	c-2-B		(torr/min.)
$^{J}/1$	-	-	-	-	1.25
$^{J}/2$	38.5	39.0	22.5	1.73	1.25
$^{J}/3$	38.2	39.5	22.3	1.77	1.25

Time of exposure to air = 16 hours

Reaction	Butene distribution			$(\frac{\text{trans}}{\text{cis}})$	Initial rate
	1-B	t-2-B	c-2-B		(torr/min.)
$K_{/1}$	42.8	31.6	25.6	1.23	1.66
$K_{/2}$	45.1	30.1	24.8	1.21	2.50
$K_{/3}$	44.1	31.9	24.0	1.33	2.50

Figure 5.10 The influence of air treatment upon the butadiene hydrogenation activity of molybdenum disulphide catalyst at 350°C.



CHAPTER 6

6. The Reaction of Buta-1,3-Diene with Hydrogen over Sulphur Treated Molybdenum Disulphide Catalysts

6.1 Introduction

In this chapter the influence of pretreatment of the catalysts with sulphur-containing compounds (either by catalyst treatment with hydrogen sulphide or by carrying out series of thiophene hydrodesulphurisation reactions) upon the behaviour of the catalysts in butadiene hydrogenation is considered.

The reactions of butadiene with hydrogen resulted in the formation of all three isomers of n-butene, namely, but-1-ene, trans-but-2-ene, cis-but-2-ene. The percentage yield of n-butane in all the reactions carried out did not exceed 1.0%, therefore the variation in the proportions of butene isomers as a result of pretreatment of the catalyst with sulphur containing compounds is mainly considered.

Unless otherwise stated, in all butadiene hydrogenations described in this chapter, the following standard experimental conditions were used.

Temperature, $350.0 \pm 2.0^{\circ}C$

Initial pressures:

Butadiene 50.0 ± 1.0 torr

Hydrogen 150.0 ± 2.0 torr

6.2 The pressure against time curves

Figure 6.1 shows a typical pressure fall against time curve for the reaction under standard conditions over 1.00g molybdenum disulphide catalyst which had been treated by carrying out a series of seven hydrodesulphurisation reactions at 350.0 ± 2.0°C. Also shown in figure 6.1 are the function plots to test for a first or second order reaction. It can be seen that the graph showed an order intermediate between first and second.

The pressure fall against time curves over the fresh sample of catalyst and over this sulphur treated catalyst were identical as may be seen by comparing figure 6.1 with that of figure 5.1 in chapter 5.

6.3 The influence of sulphur compounds and methods of sulphur treatment on catalytic behaviour of molybdenum disulphide catalysts

The purpose of performing the following experiments was twofold, namely

(a) to investigate the effect on the catalyst of sulphur treatment (with sulphur introduced either by catalyst treatment with hydrogen sulphide or by carrying out thiophene hydrodesulphurisation reactions) on its performance in the catalysis of butadiene hydrogenation.

(b) the modification of the catalytic function (activity or the product distribution) when the catalyst was quantitatively treated with hydrogen sulphide.

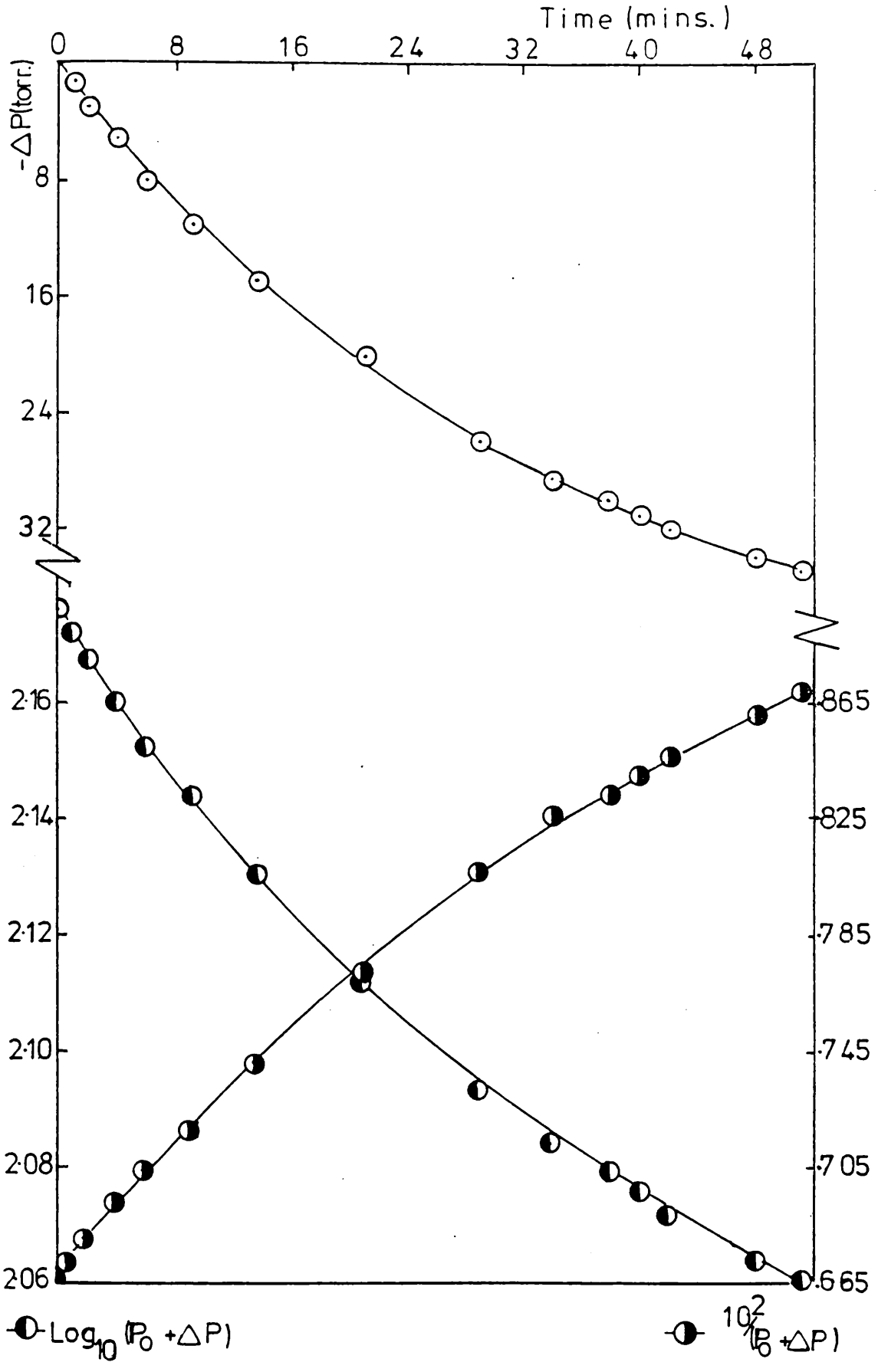


Figure 6.1 A typical pressure fall against time curve for the reaction of 50 torr of butadiene with 150 torr of hydrogen at 350°C. Also shown are the plots to test for first and second order.

Series A

A series of five standard butadiene hydrogenation reactions was carried out over a fresh sample of catalyst weighing 1.00g. Throughout series A, products were analysed after a pressure fall of 20 ± 0.5torr. The variation of butene distribution over the fresh catalyst was similar to that described in section 5.8 series G. The variation of initial rate and of butene distribution with the number of reactions performed over the fresh catalyst is given in table 6.1a.

The catalyst was then treated with hydrogen sulphide (17.0torr) at 350°C for 30 minutes. No quantitative measure of hydrogen sulphide uptake was made at this stage, as the aim of treating the catalyst with a large excess of hydrogen sulphide was to observe any variation in catalytic function. The catalyst was evacuated at 350°C for 30 minutes, and a further six standard butadiene hydrogenation reactions were carried out over the treated catalyst, under similar experimental conditions to those used with fresh catalyst. The dominant feature to emerge from the product analysis is the change in the butene distribution, compared to the distribution observed over the fresh catalyst. It can be seen from figure 6.2 that the trans-but-2-ene yield increases at the expense of the but-1-ene yield, although there was no significant change in the cis-but-2-ene yield. The variation of the initial rate and the butene distribution with the

reaction number over the treated catalyst is given in table 6.1b. The treatment of the catalyst with hydrogen sulphide also resulted in an increase in the initial rate of reaction (figure 6.2). The activity, however, diminished gradually with the number of reactions performed until it had decreased to the activity of the catalyst before hydrogen sulphide treatment. The catalyst was treated with a further quantity of hydrogen sulphide (20.0torr) at 350^{o}C for 45 minutes and then evacuated at the same temperature for 30 minutes. A further series of six standard butadiene hydrogenation reactions was then carried out. The butene distribution after the second hydrogen sulphide treatment was similar to that observed after the first treatment with hydrogen sulphide. However, the activity, after first being enhanced, achieved the steady state after fewer hydrogenation runs, than was the case after the first hydrogen sulphide treatment. This variation of the butene distribution and the activity after the second hydrogen sulphide treatment is shown in table 6.1c. When the catalyst was treated with further samples of hydrogen sulphide under similar conditions, no further effect on either the activity or the butene distribution was observed. The results of these series are given in tables 6.1d and 6.1e.

Table 6.1

The influence of hydrogen sulphide over the initial rate and the butene distribution (series A)

Weight of the catalyst = 1.00g.

Table 6.1a Reactions over the fresh catalyst

Reaction	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
A/1	46.4	38.0	15.6	2.44	0.866	1.50
A/2	56.8	28.4	14.8	1.92	1.315	4.00
A/3	62.3	25.9	11.8	2.19	1.653	3.00
A/4	58.7	24.9	16.4	1.52	1.421	2.00
A/5	59.3	24.6	16.1	1.53	1.457	1.50

Table 6.1b After first hydrogen sulphide treatment

Reaction	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
A/6	43.9	42.1	14.0	3.01	0.783	5.00
A/7	39.7	44.0	16.3	2.70	0.658	3.00
A/8	36.9	45.8	17.3	2.65	0.585	1.50
A/9	35.1	44.6	20.3	2.20	0.541	1.50
A/10	35.9	44.4	19.7	2.25	0.560	1.00
A/11	38.3	44.2	17.5	2.52	0.621	1.00

Table 6.1c After second hydrogen sulphide treatment

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate
	1-B	t-2-B	c-2-B			(torr/min.)
A/12	40.5	44.7	14.8	3.02	0.681	3.00
A/13	33.2	46.6	20.2	2.31	0.497	1.00
A/14	36.5	46.4	17.1	2.71	0.575	0.80
A/15	33.5	48.3	18.2	2.65	0.504	0.50
A/16	33.9	47.5	18.6	2.55	0.513	0.50
A/17	33.6	48.3	18.1	2.67	0.506	0.50

Table 6.1d After third hydrogen sulphide treatment

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate
	1-B	t-2-B	c-2-B			(torr/min.)
A/18	33.7	44.9	21.4	2.10	0.508	0.50
A/19	35.6	48.3	16.1	3.00	0.553	0.50
A/20	31.9	47.1	21.0	2.24	0.468	0.50
A/21	29.9	49.9	20.2	2.47	0.427	0.25
A/22	33.5	48.1	18.4	2.61	0.504	0.25
A/23	33.0	46.5	20.5	2.27	0.493	0.50

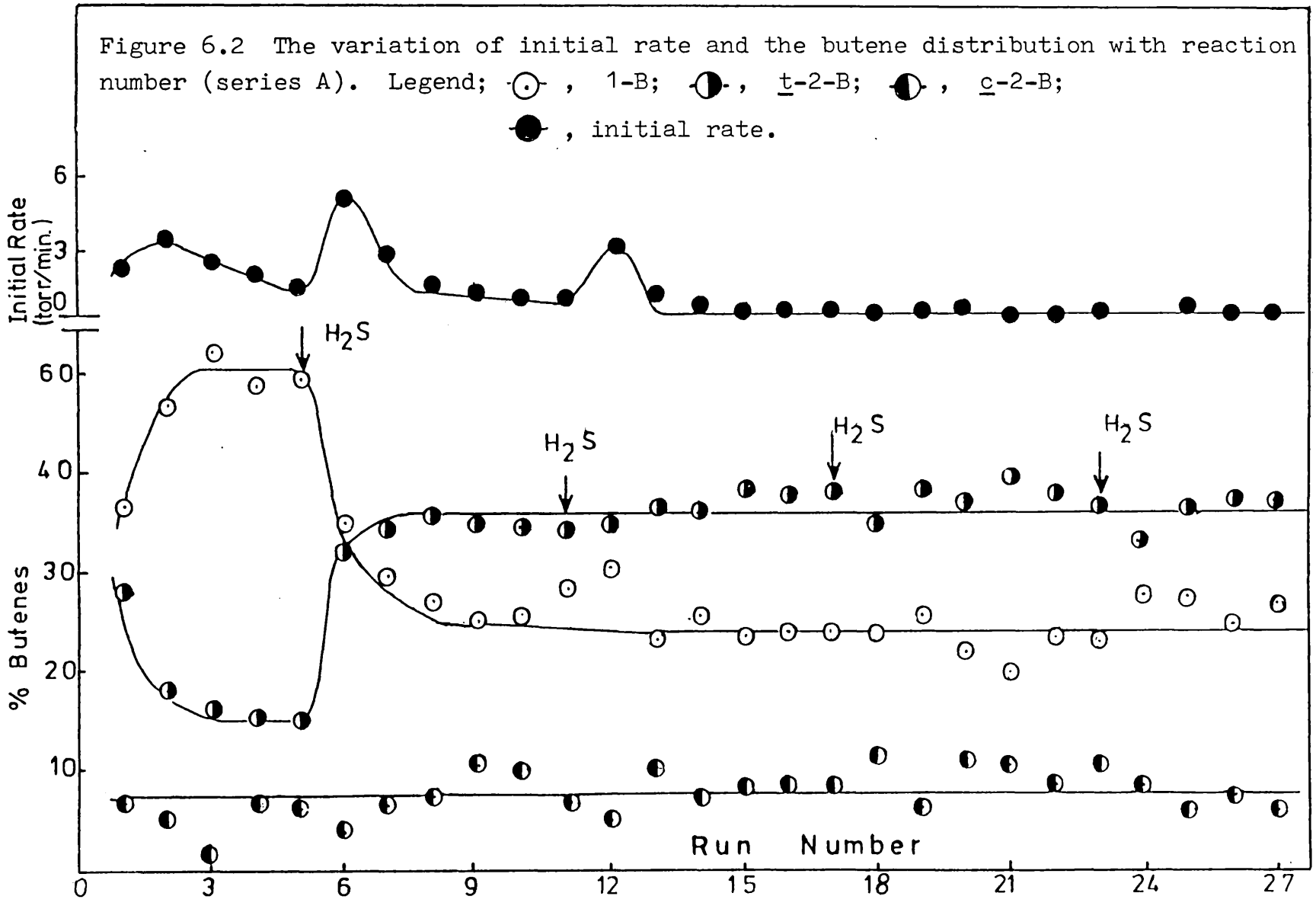


Figure 6.2 The variation of initial rate and the butene distribution with reaction number (series A). Legend; ⊙, 1-B; ◑, t-2-B; ◐, c-2-B; ●, initial rate.

Table 6.1e After fourth hydrogen sulphide treatment

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
A/24	38.3	43.3	18.4	2.35	0.621	0.80
A/25	37.8	46.5	15.7	2.96	0.608	0.50
A/26	34.9	47.7	17.4	2.74	0.536	0.44
A/27	36.8	47.3	15.9	2.97	0.582	0.36
A/28	28.2	44.9	26.9	1.67	0.393	0.40

Series B

In series A, the catalyst was treated with a large excess of hydrogen sulphide and the results demonstrated that this treatment led to changes in the activity and in the butene distribution. No quantitative estimation was made of sulphur uptake, which was responsible for the total change in the catalytic function.

In this series of reactions, the results are given of experiments where a sample of catalyst B, weighing 0.576g, was treated successively with known amounts of hydrogen sulphide, and the gradual change in catalytic behaviour was observed as a function of hydrogen sulphide uptake, as follows.

A series of butadiene hydrogenation experiments was first carried out over the fresh catalyst. Throughout series B,

the products were analysed at a pressure fall of 10.0 ± 0.5 torr. The results are given in table 6.2a. The butene distribution showed a similar trend to that observed in the series A reactions presented in table 6.1a.

The catalyst was then treated with a known quantity of hydrogen sulphide at 350°C for about 30 minutes. Any residual hydrogen sulphide in the gas phase was then quantitatively transferred to the gas chromatograph so that it could be measured. The catalyst was evacuated for 15 minutes, at the same temperature. A series of eight buta-1,3-diene hydrogenation reactions was carried out under standard conditions over the catalyst after this treatment. The results showed that the small amount of hydrogen sulphide uptake resulted in a change in the butene distribution - that is there was a small decrease in the yield of but-1-ene and an increase in the yield of trans-but-2-ene. However, there was no marked trend in the butene distribution with the number of reactions performed. The treatment with hydrogen sulphide also caused an increase in the initial rate of reaction at first. The activity however gradually diminished with the number of reactions performed. Several further treatments of the catalyst with known amounts of hydrogen sulphide were made, and a series of butadiene hydrogenations was carried out after each treatment. A gradual change in the butene distribution was observed. There was a limit to the change in activity and the butene distribution as a function of total uptake of

hydrogen sulphide, although hydrogen sulphide uptake continued after this limit had been reached. The results are given in table 6.2b.

The catalyst was treated with three changes of hydrogen (~250torr) at 350^{o}C for a total period of 17 hours. The catalyst treatment with hydrogen was done to see if any removal of the sulphur, which had been introduced as hydrogen sulphide, would occur, thereby restoring the catalyst function towards its original state. After each hydrogen treatment the catalyst was investigated for butadiene hydrogenation reactions. The results given in table 6.2c showed that there was no marked variation in the butene distribution or in the initial rate of reaction after each hydrogen treatment. A further treatment with hydrogen (~200 torr) at a higher temperature (500^{o}C) for three hours again did not influence either the butene distribution or the initial rate of reaction (table 6.2d).

No hydrogen sulphide was observed in the analysis of the reaction products either after catalyst treatment with hydrogen or as a result of carrying out series of butadiene hydrogenation reactions over the sulphur treated catalyst.

Figure 6.3 shows the variation of butene distribution and the initial rate of reaction with reaction number in series B.

The variation of butene distribution (an averaged value for individual butenes for a single set of reactions), against the amount of hydrogen sulphide uptake is shown in figure 6.4.

Table 6.2

Weight of the catalyst = 0.5769

Table 6.2a The variation of the butene distribution over the fresh catalyst

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
$^{B}/_{1}$	30.3	43.9	25.8	1.70	0.435	1.50
$^{B}/_{2}$	51.7	32.7	15.6	2.10	1.07	2.40
$^{B}/_{3}$	56.4	27.8	15.8	1.76	1.29	1.50
$^{B}/_{4}$	58.3	27.6	14.1	1.96	1.40	1.43
$^{B}/_{5}$	58.7	27.0	14.3	1.89	1.42	1.11

Table 6.2b The variation of initial rate of reaction and butene distribution with increasing sulphur uptake

The amount of hydrogen sulphide uptake = 2.60 μm
(complete uptake of sample)

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate
	1-B	t-2-B	c-2-B			(torr/min.)
$^{B}/_{6}$	53.0	33.4	13.6	2.46	1.13	1.11
$^{B}/_{7}$	56.7	33.1	10.2	3.24	1.31	0.63
$^{B}/_{8}$	54.5	32.9	12.6	2.61	1.20	0.63
$^{B}/_{9}$	52.5	29.0	18.5	1.57	1.11	0.43
$^{B}/_{10}$	48.3	32.3	19.4	1.66	0.934	0.43
$^{B}/_{11}$	55.2	33.9	10.9	3.11	1.23	0.50
$^{B}/_{12}$	51.2	34.4	14.4	2.39	1.05	0.36

The amount of hydrogen sulphide added to the catalyst = 3.73 μm

Hydrogen sulphide uptake = 3.73 μm

Total amount of hydrogen sulphide uptake = 6.33 μm

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate
	1-B	t-2-B	c-2-B			(torr/min.)
$^{B}/_{13}$	41.7	39.1	19.2	2.04	0.715	1.00
$^{B}/_{14}$	47.5	37.4	15.1	2.48	0.905	0.83
$^{B}/_{15}$	44.7	37.3	18.0	2.07	0.808	0.33
$^{B}/_{16}$	46.4	36.6	17.0	2.15	0.866	0.30

Table 6.2b continued

The amount of hydrogen sulphide added to the catalyst = 6.57 μm

Hydrogen sulphide uptake = 0.59 μm

Total amount of hydrogen sulphide uptake = 6.92 μm

Reaction	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
$^{B}/17$	42.2	44.5	13.3	3.35	0.730	0.50
$^{B}/18$	34.8	41.6	23.6	1.76	0.534	0.50

The amount of hydrogen sulphide added to the catalyst = 7.22 μm

Hydrogen sulphide uptake = 0.28 μm

Total amount of hydrogen sulphide uptake = 7.20 μm

Reaction	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
$^{B}/19$	37.8	44.3	17.9	2.47	0.608	0.60
$^{B}/20$	36.0	44.2	19.8	2.23	0.563	0.55
$^{B}/21$	39.4	43.6	17.0	2.56	0.650	0.55

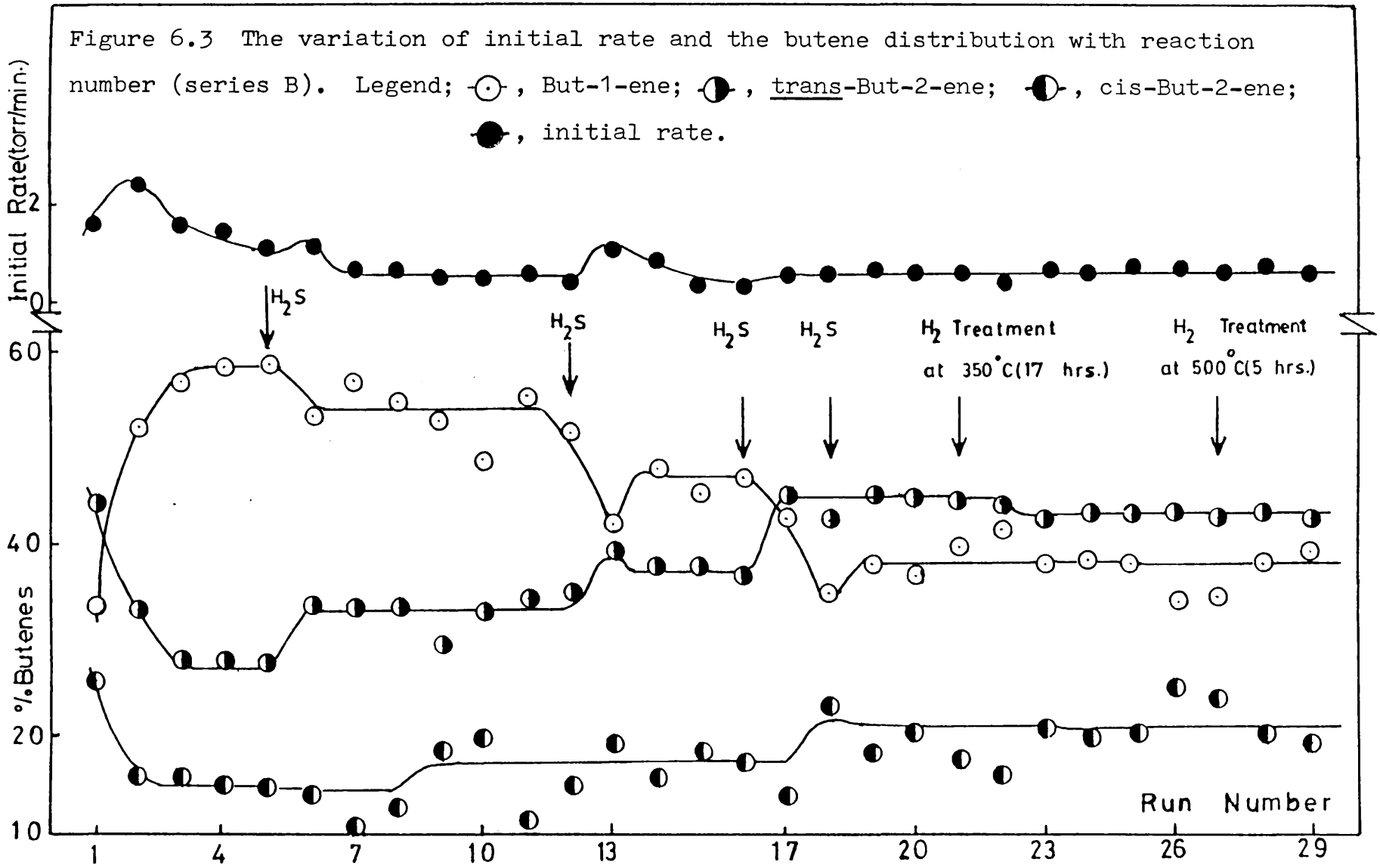
Table 6.2c The variation of butene distribution over hydrogen treated catalyst at 350°C

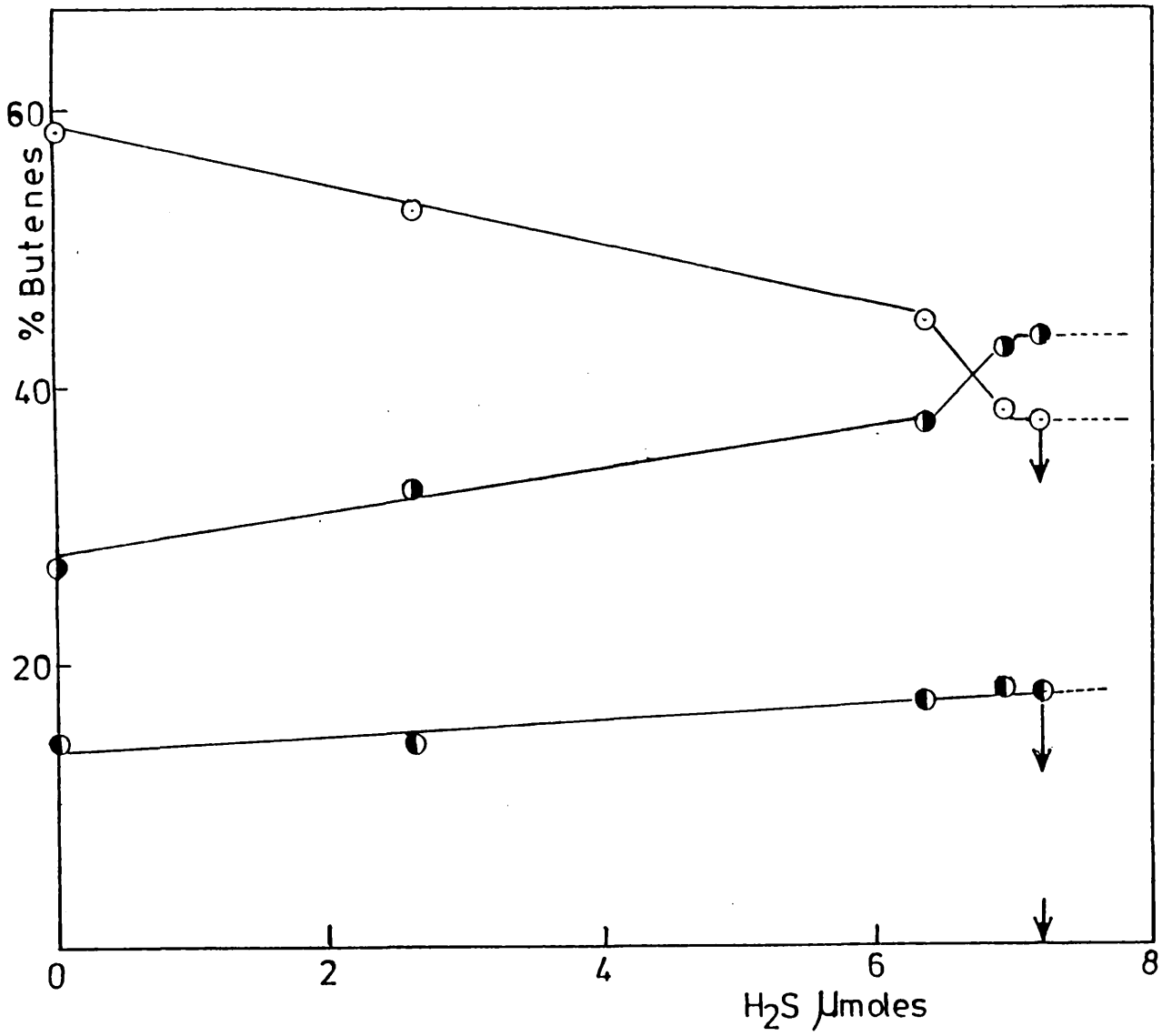
Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
B/22	41.3	43.3	15.4	2.81	0.704	0.32
B/23	37.8	41.7	20.5	2.03	0.608	0.60
B/24	37.9	42.5	19.6	2.17	0.610	0.50
B/25	37.8	42.2	20.0	2.11	0.608	0.65
B/26	33.4	42.2	24.4	1.73	0.501	0.61
B/27	33.9	42.3	23.8	1.78	0.513	0.54

Table 6.2d The variation of butene distribution over hydrogen treated catalyst at 500°C

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
B/28	37.1	42.9	20.0	2.14	0.590	0.65
B/29	39.5	41.8	18.7	2.23	0.653	0.50

Figure 6.3 The variation of initial rate and the butene distribution with reaction number (series B). Legend; ⊙, But-1-ene; ◑, trans-But-2-ene; ◐, cis-But-2-ene; ●, initial rate.





⊙ But-1-ene

◑ trans-But-2-ene

◐ cis-But-2-ene

← H_2S-uptake to achieve maximum change in the butene distribution.

Figure 6.4 The variation of butene distribution with increasing uptake of hydrogen sulphide over molybdenum disulphide at 350°C (series B)

Series C

In this series of butadiene hydrogenation reactions the catalytic activity was examined at three stages of treatment viz:

(a) the fresh evacuated catalyst was treated with excess hydrogen sulphide, followed by a series of butadiene hydrogenations. The catalyst was then treated with hydrogen, after which a further series of butadiene reactions was carried out.

It was concluded from the previous series (A and B) that treatment of the fresh catalyst with hydrogen sulphide modified its catalytic function. Furthermore, when fresh catalyst was used in the butadiene reactions, the product distribution varied over several experiments before attaining a steady state, whereas a fresh catalyst pretreated with hydrogen attained this steady state almost immediately (chapter 5.). To investigate the possibility that this behaviour arose because of surface oxygen.

(b) the catalyst was air treated to determine if the catalyst function would return towards its original state as in the fresh evacuated catalyst.

Finally,

(c) this catalyst was again treated with hydrogen sulphide to compare and contrast the effect of sulphur treatment at stages (a) and (c).

The experimental details of series C reactions were as follows. A fresh sample of catalyst C weighing 1.00g was

heated <u>in vacuo</u> up to 350°C for 30 minutes, treated with a large excess of hydrogen sulphide (20.0torr) at 350°C for one hour and then evacuated for 30 minutes. A series of eight butadiene hydrogenation reactions was carried out over the treated catalyst. Throughout this series the products were analysed after a pressure fall of 20torr. The variation of butene distribution and the initial rate of reaction is given in table 6.3a. The results show that the butene distribution was somewhat similar to that found over the catalyst A (which had been used for butadiene hydrogenation <u>before</u> hydrogen sulphide treatment). The catalytic activity over catalyst C after the treatment was ~19.0 torr/min. (reaction $C_{/1}$), which was markedly higher than that observed over catalyst A (5.0 torr/min., reaction $A_{/6}$).

This catalyst was then treated with two changes of hydrogen (~200torr) at 420°C for a total period of ten hours. The catalyst was evacuated at the same temperature for 15 minutes and the temperature lowered to 350°C. A further eight butadiene hydrogenation reactions were carried out under similar conditions to those used previously. The variation of the butene distribution and the initial rate of reaction with the number of reactions performed after this treatment is given in table 6.3b. The results reveal that treating the catalyst with hydrogen caused no change in the butene distribution. Nor did this vary with reaction number.

Interesting results were obtained from the situation,

when the catalyst was exposed to air (100torr) at 350°C for one hour followed by evacuation at 350°C for 30 minutes. A series of five butadiene hydrogenation reactions was performed over the air treated catalyst, when a marked change in the catalytic function was observed. The percentage of butene distribution shows that the but-1-ene increased while the trans-but-2-ene and the cis-but-2-ene yield decreased as a result of the air treatment. However, no change was observed in the activity of the catalyst after this treatment. The results for this series of reactions are given in table 6.3c.

An interesting feature to emerge from this series (table 6.3c) of reactions is that the butene distribution was similar to that observed over the fresh sample of catalyst which was treated with hydrogen followed by air treatment (chapter 5 table 5.8).

Further treatment of the catalyst with hydrogen (200torr) at 350°C for a period of four hours did not cause the butene distribution to change relative to the previous set of experiments (table 6.3c) although this treatment resulted in a marked increase in the reaction rate. The activity however diminished gradually with the number of reactions performed (table 6.3d).

This catalyst was then treated with hydrogen sulphide (~ 20torr) at 350°C for 30 minutes and evacuated at the same temperature for another 15 minutes. A series of four buta-diene hydrogenation reactions was carried out over the treated

catalyst. The results show that as a consequence of this hydrogen sulphide treatment, the but-1-ene yield decreased and the trans-but-2-ene and the cis-but-2-ene yield increased (table 6.3e). From the results it can be seen that the butene distribution is independent of the number of reactions performed. The activity was slightly enhanced at first as a result of the hydrogen sulphide treatment, but diminished with the reaction number. Comparing results given in the tables 6.3a and 6.3e, it can be seen that the butene distribution is similar in both series of reactions. However, a marked difference can be seen in the initial activity after the hydrogen sulphide treatment.

The variation of the butene distribution and the activity of the catalyst C with the number of reactions carried out after each treatment is shown in figure 6.5. The dotted lines drawn in the figure represent the variation of butene distribution and the initial rate of reaction over the fresh evacuated catalyst as deduced from earlier results in series A and B.

Table 6.3

The reaction of buta-1,3-diene with hydrogen over catalyst C (Series C)

Weight of the catalyst = 1.00g.

Table 6.3a The variation of inital rate and butene distribution over the catalyst pretreated with hydrogen sulphide

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
C/1	28.3	52.7	19.0	2.77	0.395	18.18
C/2	27.9	52.3	19.8	2.64	0.387	16.00
C/3	29.2	49.8	21.0	2.37	0.412	14.00
C/4	24.5	49.5	26.0	1.90	0.324	14.00
C/5	25.6	51.2	23.2	2.21	0.344	13.00
C/6	28.1	50.1	21.8	2.30	0.391	12.00
C/7	29.2	52.3	18.5	2.83	0.412	9.00
C/8	30.4	50.0	19.6	2.55	0.437	9.00

Table 6.3b The variation of inital rate and the butene distribution over the hydrogen treated catalyst

After first hydrogen treatment at 420°C

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
C_9	30.5	48.6	20.9	2.33	0.439	8.00
C_{10}	27.3	49.6	23.1	2.15	0.376	5.00
C_{11}	27.8	51.4	20.8	2.47	0.385	4.00
C_{12}	27.8	51.7	20.5	2.52	0.385	3.00
After second hydrogen treatment at 420°C						
C_{13}	30.8	49.3	19.9	2.47	0.445	5.00
C_{14}	28.9	50.7	20.4	2.49	0.406	3.00
C_{15}	27.7	51.5	20.8	2.48	0.383	4.00
C_{16}	28.5	51.2	20.3	2.52	0.399	3.00

Table 6.3c The inital rate of reaction and the butene distribution over the air treated catalyst

Reaction	Butene distribution 1-B	t-2-B	c-2-B	(trans/cis)	1-B/2-B	Initial rate (torr/min.)
C/17	60.1	26.8	13.1	2.05	1.51	3.50
C/18	65.0	25.8	9.2	2.80	1.86	1.50
C/19	60.9	26.4	12.7	2.08	1.56	1.00
C/20	63.9	25.3	10.8	2.34	1.77	1.00
C/21	66.1	24.8	9.1	2.73	1.95	2.00

Table 6.3d After hydrogen treatment at 350°C

Reaction	Butene distribution 1-B	t-2-B	c-2-B	(trans/cis)	1-B/2-B	Initial rate (torr/min.)
C/22	60.4	29.3	10.3	2.84	1.53	12.00
C/23	62.8	27.6	9.6	2.87	1.69	7.00
C/24	60.6	28.0	11.4	2.46	1.54	7.00
C/25	63.8	26.9	9.3	2.89	1.76	5.00

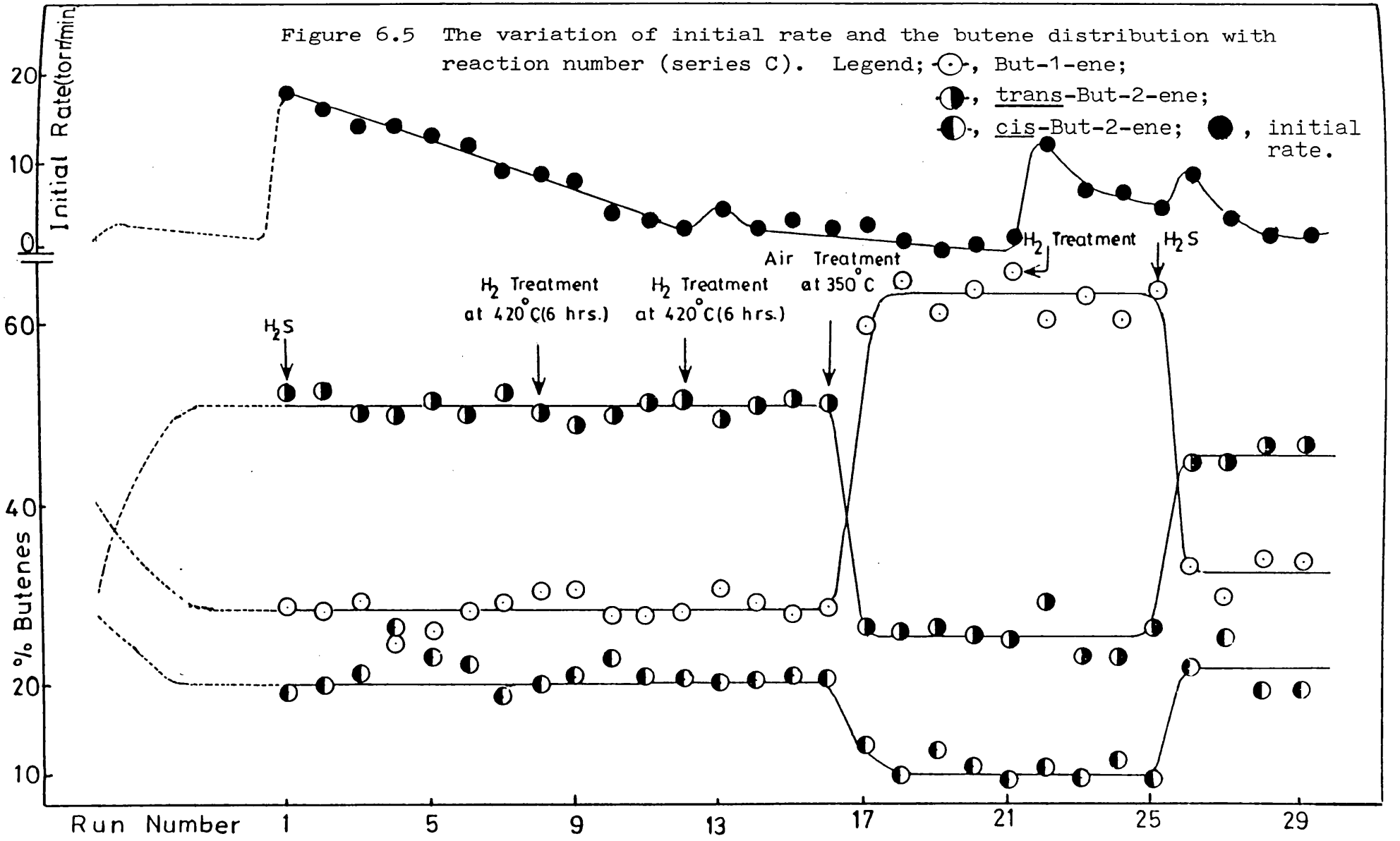


Figure 6.5 The variation of initial rate and the butene distribution with reaction number (series C). Legend; ⊙, But-1-ene; ◑, trans-But-2-ene; ◐, cis-But-2-ene; ●, initial rate.

Table 6.3e After hydrogen sulphide treatment at 350°C

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
C/26	33.7	44.8	21.5	2.08	0.508	8.00
C/27	29.7	45.3	25.0	1.81	0.422	4.00
C/28	34.2	46.8	19.0	2.46	0.520	2.50
C/29	34.0	46.4	19.6	2.37	0.515	2.00

Series D

In series C, the fresh sample of catalyst was treated with a large excess of hydrogen sulphide and the results revealed that this treatment led to changes in the catalytic function. No quantitative estimation was made of sulphur uptake, which was responsible for the total change in catalytic behaviour.

The work described in this series is concerned with the use of [^{35}S]-hydrogen sulphide. [^{35}S]-labelled hydrogen sulphide was used to determine the extent of possible sulphur exchange between the surface and the gas phase. In a situation where the catalyst was treated with [^{35}S]-hydrogen sulphide, the possible displacement of [^{35}S]-hydrogen sulphide or its production by treatment with hydrogen or as a result of butadiene hydrogenation reactions could be observed at standard conditions and

the reactions were analysed at a pressure fall of 10.0 torr.

A fresh sample of catalyst (0.5704g) was treated with [^{35}S]-labelled hydrogen sulphide (4.63 μm) at 350°C, then evacuated at the same temperature for about 30 minutes. A series of butadiene hydrogenation reactions was carried out over the treated catalyst. The trend in the butene distribution with the reaction number was similar to that observed over the fresh evacuated catalyst described for series A, table 6.1a and series B, table 6.2a. The catalyst was then quantitatively treated with further amounts of [^{35}S]-hydrogen sulphide and a series of butadiene hydrogenation reactions performed after each [^{35}S]-hydrogen sulphide uptake. A systematic change in the butene distribution was observed, which was similar to that found in series B, table 6.2b. The results, after each stage of sulphur treatment for this series are shown in table 6.4a and figure 6.6. Also shown, in figure 6.7, is the dependence of the butene distribution with the amount of sulphur uptake.

The catalyst was treated with hydrogen (~300 torr) at 500°C for five hours, evacuated at the same temperature for about 15 minutes, then the temperature was lowered to 350°C. A further series of butadiene hydrogenation reactions was then performed. The variation of butene distribution with the number of reactions performed over the hydrogen treated catalyst is shown in table 6.4b. The activity was increased at first but gradually decreased with the reaction number.

The catalyst was exposed to air (25.0 torr) at 350°C for one hour and then evacuated at the same temperature for 30 minutes. Two butadiene hydrogenation reactions were carried out. The results, given in table 6.4c, show that the but-1-ene yield increased (compared with that observed before this treatment), while the trans-but-2-ene yield decreased.

In these experiments, no [^{35}S]-hydrogen sulphide or hydrogen sulphide was obtained as the result of hydrogenation reactions or the catalyst treatment with hydrogen or air. Also no sulphur was exchanged between the surface and the gas phase at any stage of [^{35}S]-hydrogen sulphide adsorption, as shown by the observation that the specific activity of the hydrogen sulphide which was not taken up by the catalyst had not changed, i.e. had not been isotopically diluted by inactive sulphur from the catalyst.

Table 6.4

Weight of the catalyst = 0.5704g

Table 6.4a The variation of butene distribution with increasing amount of [^{35}S]-hydrogen sulphide uptake

The amount of [^{35}S]-hydrogen sulphide uptake = 4.63 μm (complete uptake of sample)

Reaction	Butene distribution			$(\frac{\text{trans}}{\text{cis}})$	$\frac{\text{1-B}}{\text{2-B}}$	Initial rate
	1-B	t-2-B	c-2-B			(torr/min.)
D/1	41.7	35.8	22.5	1.59	0.715	2.00
D/2	60.4	25.0	14.6	1.71	1.52	2.50
D/3	60.2	24.6	15.2	1.62	1.51	2.00
D/4	60.1	24.2	15.7	1.54	1.51	2.00
D/5	61.0	23.2	15.8	1.47	1.56	1.50

Table 6.4a continued

The amount of [^{35}S]-hydrogen sulphide added to the catalyst = 4.87 μm

[^{35}S]-hydrogen sulphide uptake = 4.87 μm

Total amount of [^{35}S]-hydrogen sulphide uptake = 9.50 μm

Reaction	Butene distribution 1-B	t-2-B	c-2-B	(trans/cis)	1-B/2-B	Initial rate (torr/min.)
^{D}/6	52.7	30.8	16.5	1.87	1.11	2.50
^{D}/7	55.0	29.1	15.9	1.83	1.22	2.00
^{D}/8	55.2	29.6	15.2	1.95	1.23	1.50
^{D}/9	55.2	30.1	14.7	2.05	1.23	1.50
^{D}/10	55.6	29.9	14.5	2.06	1.25	0.66
The amount of [^{35}S]-hydrogen sulphide added to the catalyst = 4.87 μm						
[^{35}S]-hydrogen sulphide uptake = 3.47 μm						
Total amount of [^{35}S]-hydrogen sulphide uptake = 12.97 μm						
^{D}/11	45.7	36.9	17.4	2.12	0.842	1.50
^{D}/12	48.8	37.2	13.9	2.68	0.949	1.00
^{D}/13	48.0	36.7	15.3	2.40	0.923	1.00
^{D}/14	46.9	36.0	17.1	2.11	0.883	0.66

Table 6.4a continued

The amount of [^{35}S]-hydrogen sulphide added to the catalyst = 4.71 μm

[^{35}S]-hydrogen sulphide uptake = 1.87 μm

Total amount of [^{35}S]-hydrogen sulphide uptake = 14.84 μm

Reaction	Butene distribution 1-B	t-2-B	c-2-B	($\frac{trans}{cis}$)	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
^{D}/15	37.7	41.4	21.0	1.97	0.605	1.00
^{D}/16	36.6	42.1	21.3	1.98	0.578	1.00
^{D}/17	38.9	41.6	19.5	2.13	0.637	1.00
The amount of [^{35}S]-hydrogen sulphide added to the catalyst = 4.55 μm						
[^{35}S]-hydrogen sulphide uptake = 1.54 μm						
Total amount of [^{35}S]-hydrogen sulphide uptake = 16.38 μm						
^{D}/18	36.1	42.6	21.3	2.00	0.565	1.00
^{D}/19	38.8	43.7	17.5	2.50	0.634	1.00
^{D}/20	35.9	42.4	21.7	1.95	0.560	1.00
The amount of [^{35}S]-hydrogen sulphide added to the catalyst = 4.51 μm						
[^{35}S]-hydrogen sulphide uptake = 2.60 μm						
Total amount of [^{35}S]-hydrogen sulphide uptake = 18.98 μm						
^{D}/21	33.8	42.3	23.9	1.77	0.511	1.00
^{D}/22	33.0	44.4	22.6	1.96	0.493	1.00

Table 6.4a continued

The amount of [^{35}S]-hydrogen sulphide added to the catalyst = 4.38 μm

[^{35}S]-hydrogen sulphide uptake = 2.11 μm

Total amount of [^{35}S]-hydrogen sulphide uptake = 21.09 μm

Reaction	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
$^{D}/_{23}$	34.2	42.2	23.6	1.79	0.520	1.00
$^{D}/_{24}$	35.0	44.9	20.1	2.23	0.538	1.00
The amount of [^{35}S]-hydrogen sulphide added to the catalyst = 4.46 μm						
[^{35}S]-hydrogen sulphide uptake = 1.06 μm						
Total amount of [^{35}S]-hydrogen sulphide uptake = 22.15 μm						
$^{D}/_{25}$	34.8	43.4	21.8	1.99	0.534	1.00

Table 6.4b The variation of initial rate and the butene distribution over hydrogen treated catalyst

Reaction	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
$^{D}/_{26}$	38.9	42.8	18.3	2.34	0.637	2.50
$^{D}/_{27}$	33.4	41.7	24.9	1.67	0.501	1.80
$^{D}/_{28}$	31.8	42.1	26.1	1.61	0.466	-

Table 6.4c The variation of butene distribution over air treated catalyst

Reaction	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
$^{D}/_{29}$	47.5	35.8	16.7	2.14	0.905	-
$^{D}/_{30}$	42.7	35.0	22.3	1.57	0.745	-

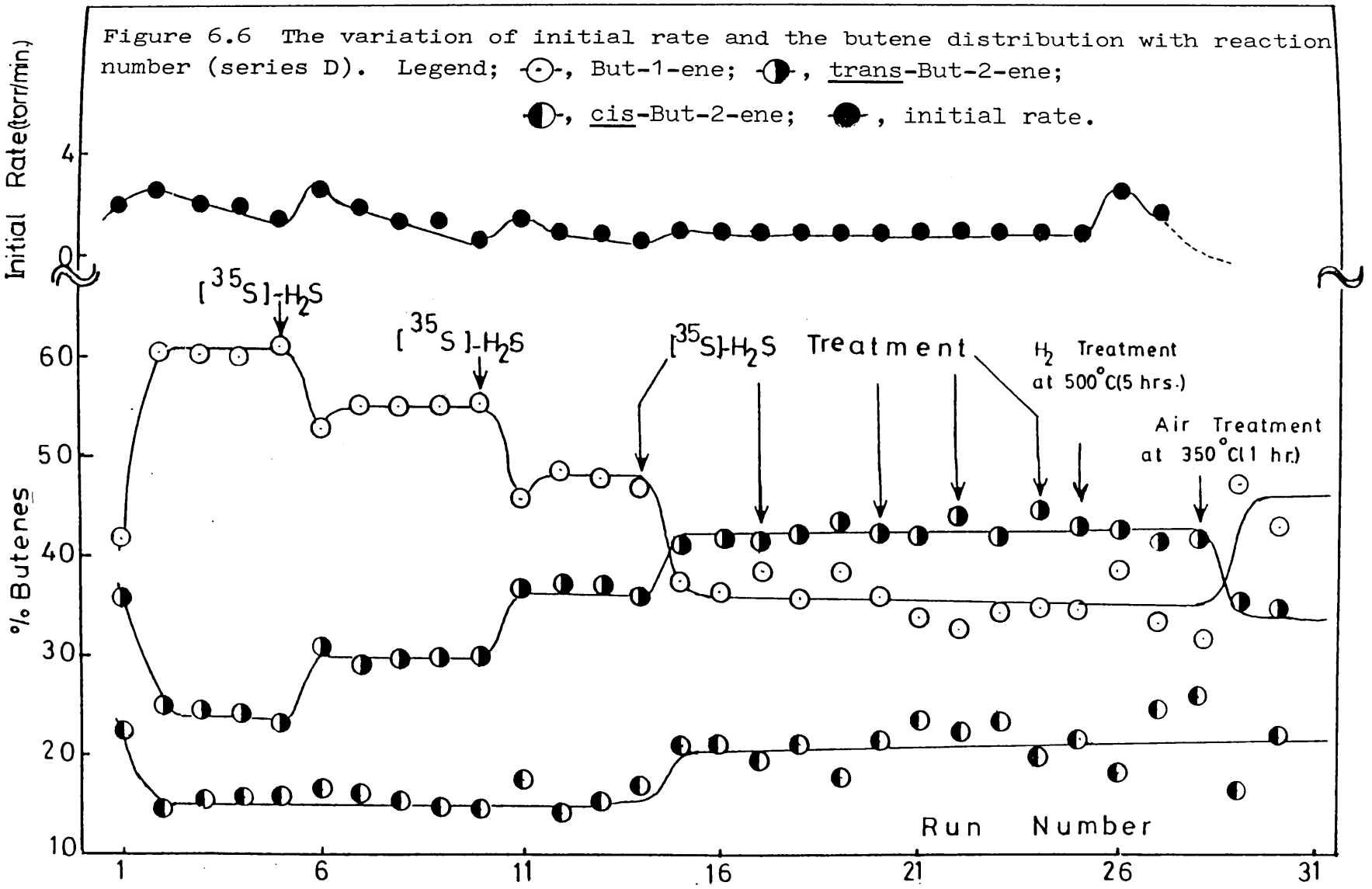
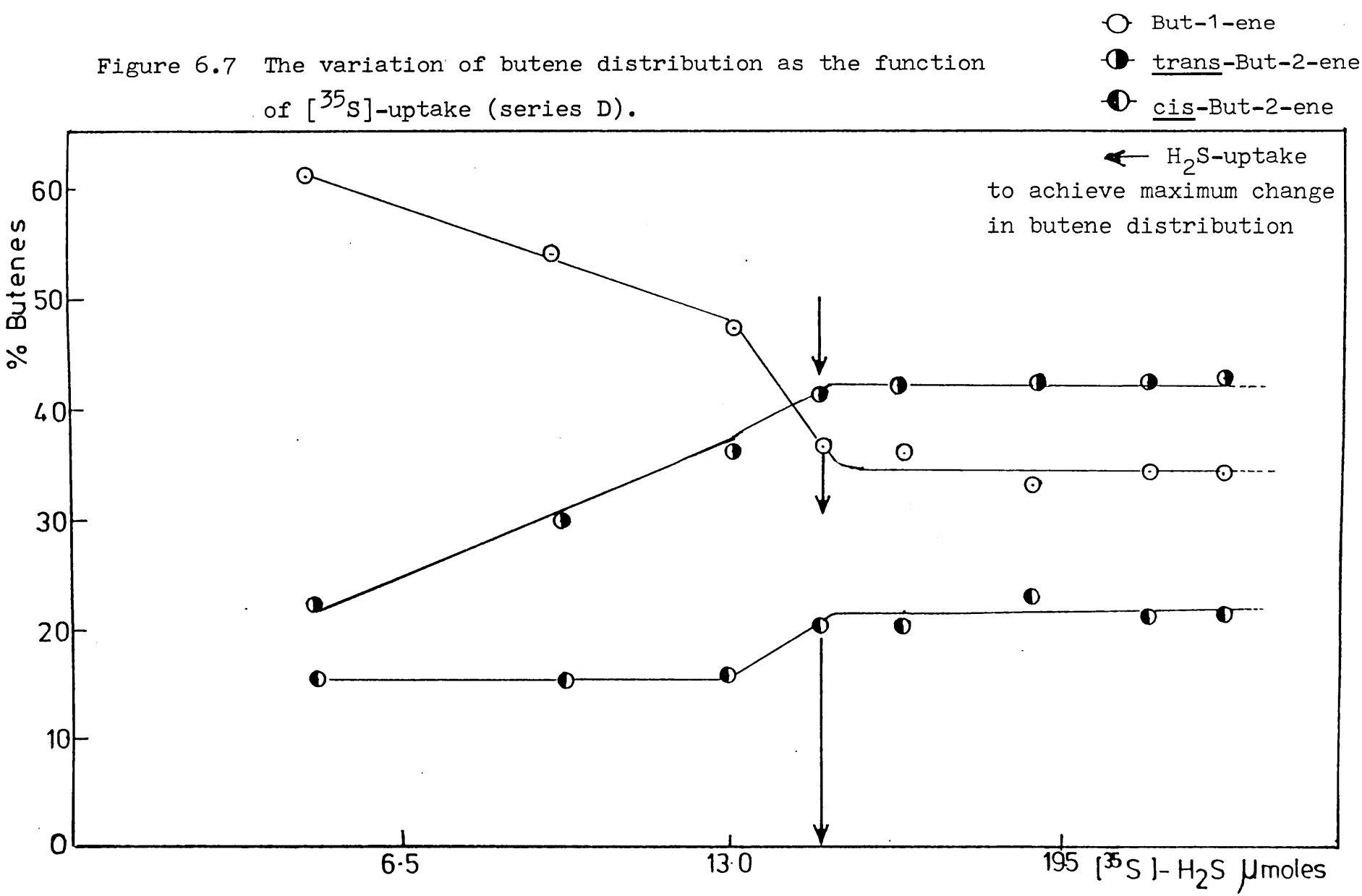


Figure 6.6 The variation of initial rate and the butene distribution with reaction number (series D). Legend; -⊙-, But-1-ene; -◑-, trans-But-2-ene; -◐-, cis-But-2-ene; -●-, initial rate.

Figure 6.7 The variation of butene distribution as the function of [^{35}S]-uptake (series D).



Series E

There were two aims in performing this series of reactions using [^{35}S]-hydrogen sulphide. First, to determine the total amount of hydrogen sulphide uptake which was necessary to achieve the maximum change in catalytic behaviour for a fresh sample of catalyst pretreated with hydrogen. Second, the use of a sulphur tracer makes it possible to determine the extent of sulphur exchange between gaseous hydrogen sulphide and surface sulphur of the molybdenum disulphide.

The experimental details of the catalyst pretreatments and the hydrogenation reactions were as follows.

A fresh sample (0.575g) of catalyst was treated with hydrogen (~ 300 torr) at 350^{o}C, for a period of four hours, then the catalyst was evacuated at the same temperature for 30 minutes. A series of butadiene hydrogenation reactions was done under similar experimental conditions to those described before in series D reactions. The butene distribution, given in table 6.5a, was constant after the first reaction, while the initial rate decreased with the number of reactions performed.

The catalyst was treated gradually with small amounts of [^{35}S]-hydrogen sulphide at 350^{o}C, followed by a series of butadiene hydrogenation reactions after each treatment. The gradual change in the butene distribution and the activity was found to be similar to that observed in series B and D.

The results for this series are shown in table 6.5b.

The catalyst was then treated with hydrogen ($\sim$ 400 torr) at 350^{o}C, for a period of 13 hours, after which the catalyst was evacuated at the same temperature for 30 minutes. Three butadiene hydrogenation experiments were then carried out. There was no marked change in the activity after this treatment. The variation of the butene distribution with the reaction number for this set of experiments is shown in table 6.5c.

It is to be noted that no hydrogen sulphide (active or inactive) was observed in the reaction products of butadiene hydrogenations, after any stage of [^{35}S]-hydrogen sulphide treatment. Similarly no hydrogen sulphide (active or inactive) was obtained when the catalyst was treated with hydrogen.

Figure 6.8 represents the butene distribution and the activity as a function of the reaction number. Also shown in figure 6.9 is the variation of the butene distribution with the amount of sulphur uptake.

Table 6.5

Weight of the catalyst = 0.575g

Table 6.5a The variation of the butene distribution with run number over a hydrogen treated catalyst

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
$E_{/1}$	58.1	25.6	16.3	1.57	1.39	8.00
$E_{/2}$	64.5	21.8	13.7	1.59	1.82	5.00
$E_{/3}$	63.4	22.1	14.5	1.52	1.73	4.00
$E_{/4}$	64.4	21.4	14.2	1.51	1.81	2.6
$E_{/5}$	-	-	-	-	-	2.11

Table 6.5b The variation of initial rate of reaction and the butene distribution with increasing uptake of [^{35}S]-hydrogen sulphide

The amount of [^{35}S]-hydrogen sulphide added to the catalyst (complete uptake of sample) = 3.98 μm

Reaction	Butene distribution 1-B	t-2-B	c-2-B	(trans/cis)	1-B/2-B	Initial rate (torr/min.)
E/6	48.5	35.6	15.9	2.24	0.942	3.00
E/7	49.7	33.9	16.4	2.07	0.988	2.00
E/8	50.4	33.0	16.6	1.99	1.02	2.00
E/9	46.5	34.5	19.0	1.82	0.869	1.25
The amount of [^{35}S]-hydrogen sulphide added to the catalyst = 4.79 μm						
[^{35}S]-hydrogen sulphide uptake = 4.79 μm						
Total amount of [^{35}S]-hydrogen sulphide uptake = 8.77 μm						
E/10	31.9	43.1	25.0	1.72	0.468	2.50
E/11	35.6	43.5	20.9	2.08	0.553	1.50
E/12	36.9	44.4	18.7	2.37	0.585	1.50
E/13	-	-	-	-	-	1.50
E/14	38.8	42.0	19.2	2.19	0.634	-

Table 6.5b continued

The amount of [^{35}S]-hydrogen sulphide added to the catalyst = 5.11 μm

[^{35}S]-hydrogen sulphide uptake = 2.19 μm

Total amount of [^{35}S]-hydrogen sulphide uptake = 10.96 μm

Reaction	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
E/15	29.8	46.4	23.8	1.95	0.424	0.92
E/16	35.2	43.8	21.00	2.09	0.543	0.55
E/17	32.2	43.9	23.9	1.84	0.475	0.55
E/18	34.9	43.8	21.3	2.06	0.536	0.55
E/19	38.7	44.4	16.9	2.63	0.631	0.50
The amount of [^{35}S]- hydrogen sulphide added to the catalyst = 3.77 μm						
[^{35}S]-hydrogen sulphide uptake = 1.85 μm						
Total amount of [^{35}S]-hydrogen sulphide uptake = 12.81 μm						
E/20	33.2	46.0	20.8	2.21	0.497	0.55
E/21	31.5	46.2	22.3	2.07	0.460	0.55
E/22	32.4	43.8	23.8	1.84	0.479	0.50
E/23	33.8	44.7	21.5	2.08	0.511	0.50
E/24	34.7	43.9	21.4	2.05	0.531	0.40

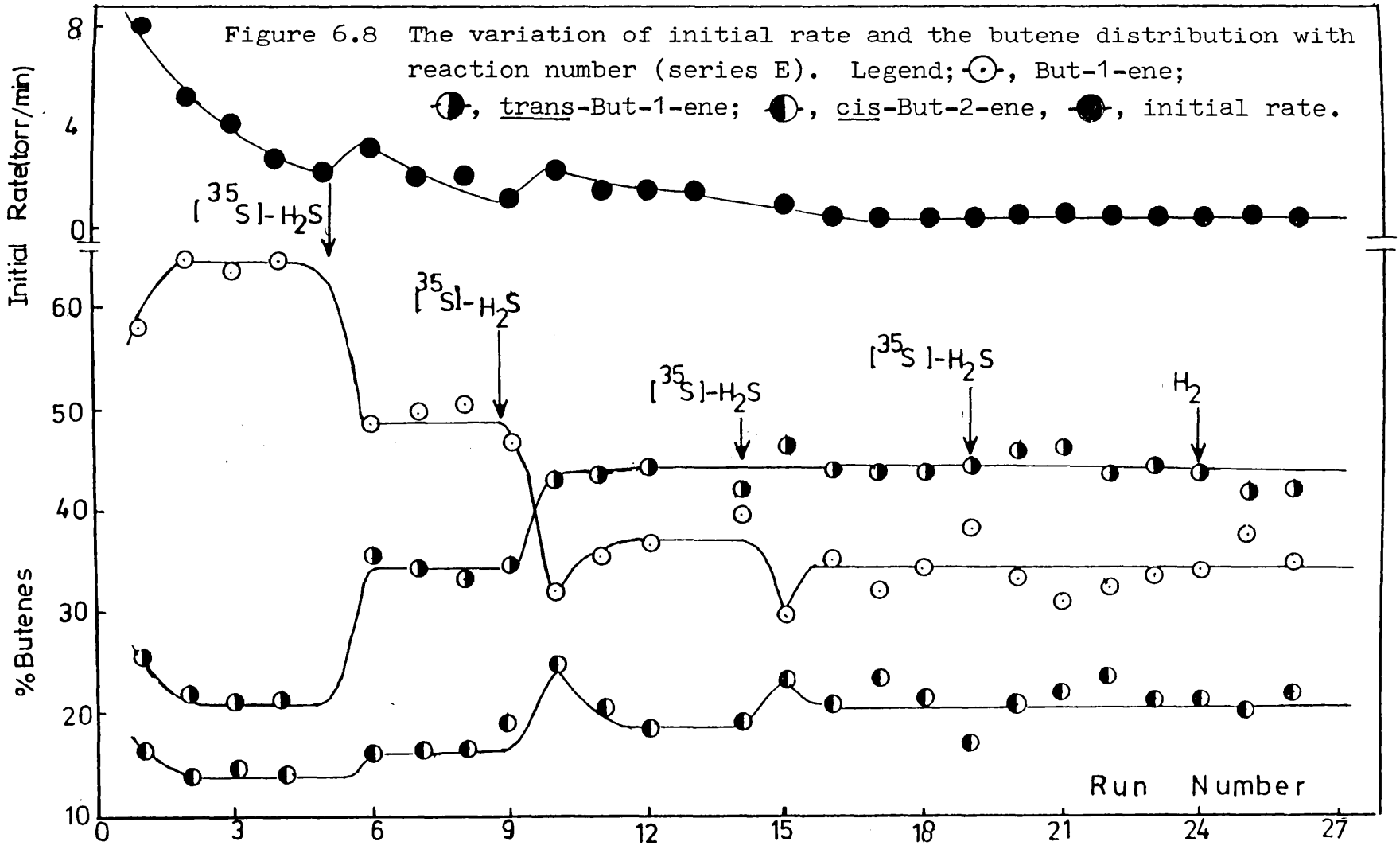


Figure 6.8 The variation of initial rate and the butene distribution with reaction number (series E). Legend; ⊙, But-1-ene; ◑, trans-But-1-ene; ◐, cis-But-2-ene, ●, initial rate.

Figure 6.9 The variation of butene distribution as the function of [^{35}S]-hydrogen sulphide uptake (series E).

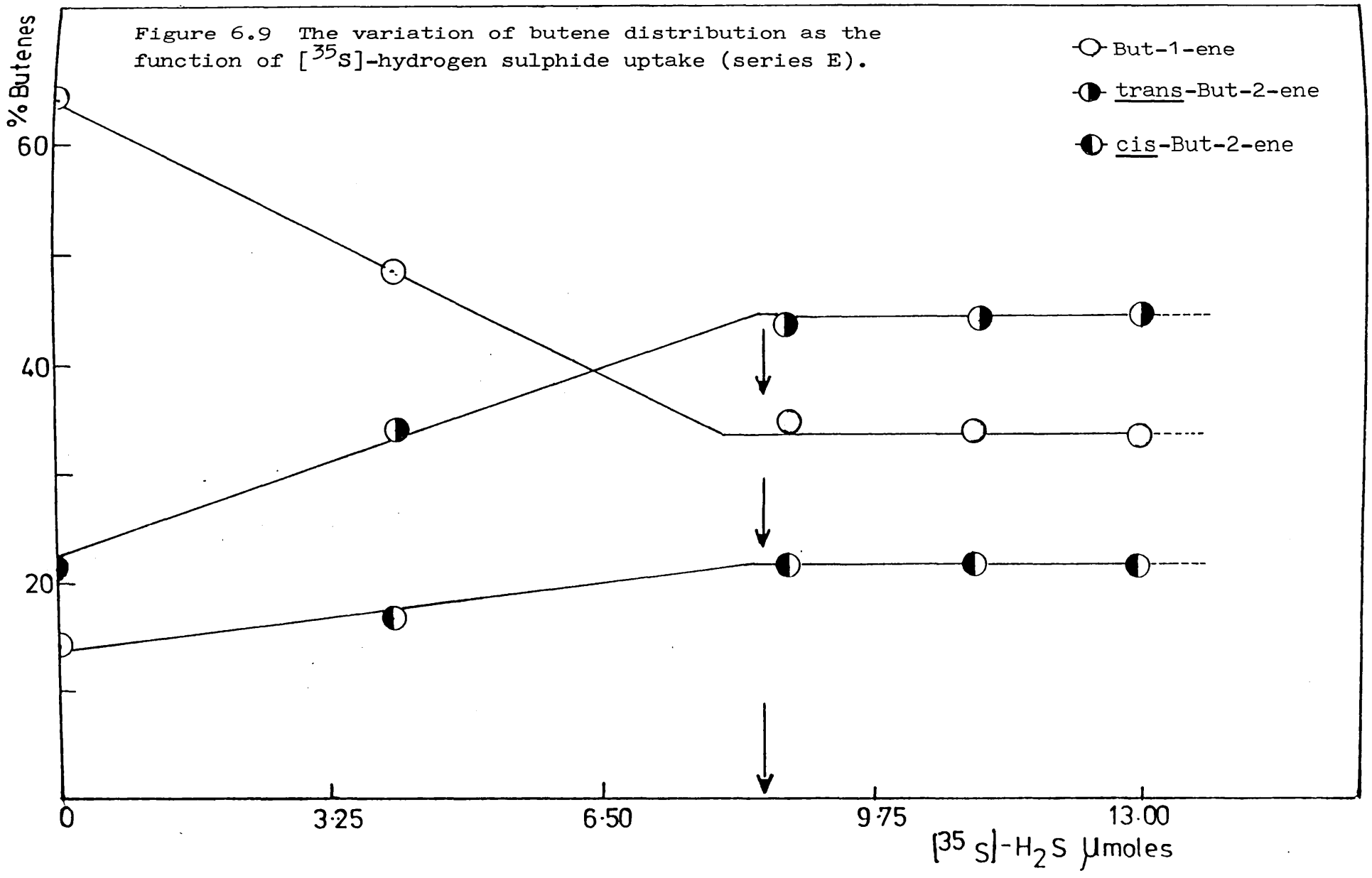


Table 6.5c Dependence of butene distribution with run number over a hydrogen treated catalyst

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
$^{E}/_{25}$	37.8	41.9	20.3	2.06	0.608	0.60
$^{E}/_{26}$	35.0	42.5	22.5	1.89	0.538	0.50
$^{E}/_{27}$	33.1	40.9	26.0	1.57	0.495	0.50

Series F

In series E, the fresh sample of catalyst was pretreated with hydrogen. In these experiments (series F) the fresh sample of catalyst was first treated with hydrogen and then exposed to air followed by a series of butadiene hydrogenation reactions. [^{35}S]-hydrogen sulphide was used to observe the possible exchange between gas phase hydrogen sulphide and the sulphur of the catalyst surface. The experimental details are described below.

A fresh sample of catalyst (0.578g) was evacuated and heated up to 350^{o}C and then treated with hydrogen ($\sim$ 400 torr) at 350^{o}C for six hours. The catalyst was evacuated at 350^{o}C and then exposed to air (20 torr) at 350^{o}C for two hours. A series of five standard butadiene hydrogenation reactions was

carried out over the treated catalyst and the products were analysed at a pressure fall of 10.0 torr. The trend in the butene distribution was similar to that found over the fresh catalyst treated with hydrogen, described in series E. The results are shown in table 6.6a.

9.74 μ moles of [^{35}S] labelled hydrogen sulphide were admitted with the catalyst at 350^{o}C and allowed to remain for one hour. The [^{35}S]-hydrogen sulphide uptake was found to be 8.85 μ moles. A series of butadiene hydrogenation experiments was done over the treated catalyst. The initial rate of reaction and the butene distribution were similar to those found over the hydrogen sulphide treated catalysts described in series A and C. The variation of the butene distribution and the initial rate of reaction with reaction number is given in table 6.6b and figure 6.10.

No hydrogen sulphide (active or inactive) was observed in the analysis of the reaction products as a result of any treatment over this catalyst.

Table 6.6

Weight of the catalyst = 0.578g

Table 6.6a The variation of the butene distribution with reaction number over a hydrogen and air treated catalyst

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate
	1-B	t-2-B	c-2-B			(torr/min.)
$F_{/1}$	48.3	27.4	24.3	1.13	0.934	5.00
$F_{/2}$	54.4	24.5	21.1	1.16	1.19	3.25
$F_{/3}$	60.6	21.8	17.6	1.24	1.54	3.00
$F_{/4}$	55.7	24.1	20.2	1.19	1.26	2.00
$F_{/5}$	54.0	25.4	20.6	1.23	1.17	2.00

Table 6.6b The variation of the butene distribution with reaction number over a [^{35}S]-hydrogen sulphide treated catalyst

The amount of [^{35}S]-hydrogen sulphide added to the catalyst = 9.74 μm

Total amount of [^{35}S]-hydrogen sulphide uptake = 8.85 μm

Reaction	Butene distribution			$(\frac{\text{trans}}{\text{cis}})$	$\frac{\text{1-B}}{\text{2-B}}$	Initial rate
	1-B	t-2-B	c-2-B			(torr/min.)
$^{F}/_{6}$	33.4	39.6	27.0	1.47	0.501	3.00
$^{F}/_{7}$	34.0	41.2	24.8	1.66	0.515	2.00
$^{F}/_{8}$	31.6	42.3	26.1	1.62	0.462	1.50
$^{F}/_{9}$	31.9	43.1	25.0	1.72	0.468	1.50

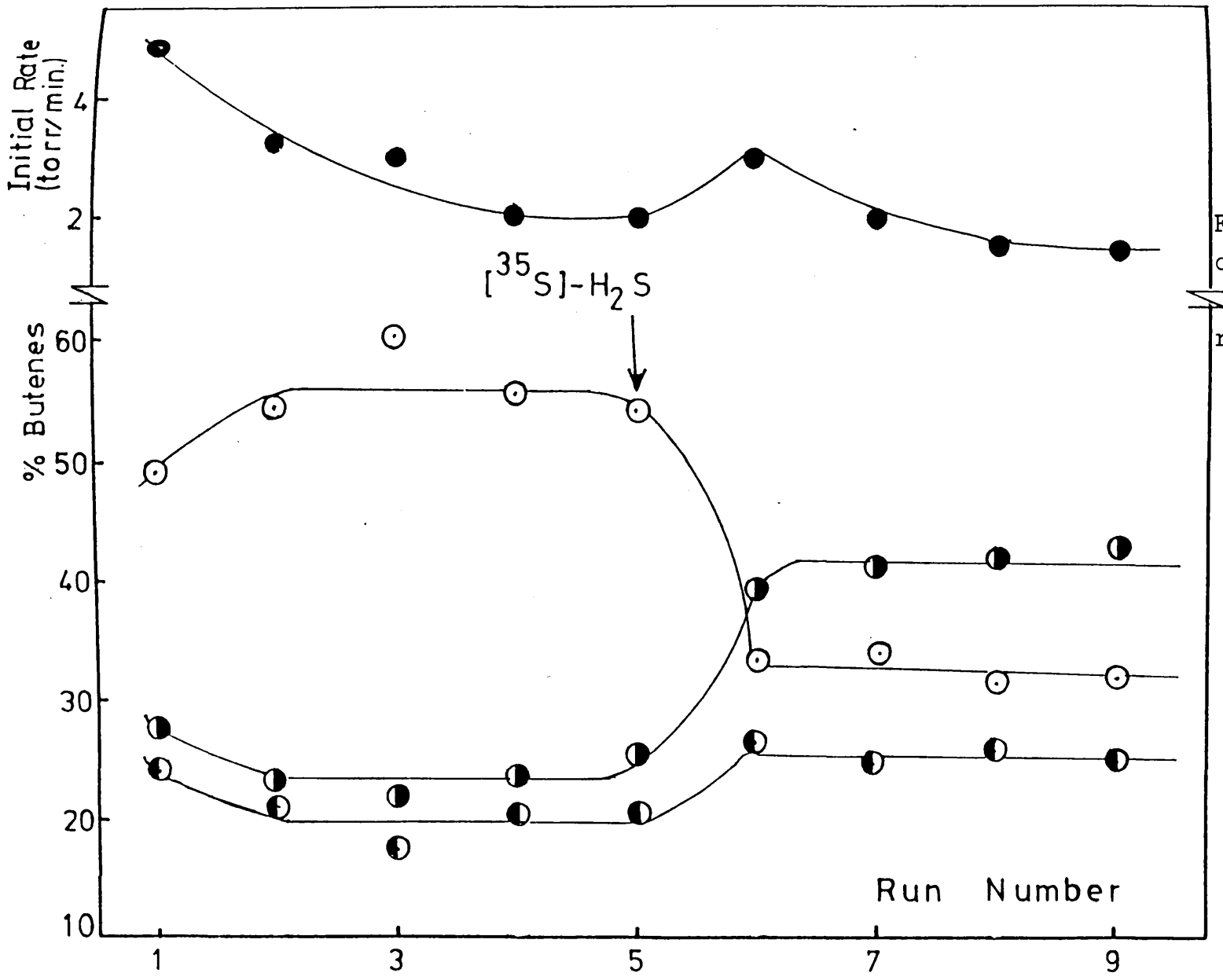


Figure 6.10 The variation of initial rate and the butene distribution with reaction number (series F).

Series G

This series is concerned with the effect of sulphur introduced to the catalyst as a consequence of thiophene hydrodesulphurisation reactions.

A fresh sample (1.002g) of catalyst was treated with two changes of a 1:4 mixture of thiophene and hydrogen (250 torr) at 350°C, for a total period of 1½ hours. The products of the thiophene hydrodesulphurisation reaction were not analysed at this stage. The catalyst was evacuated at 350°C for 30 minutes and a series of five butadiene hydrogenation reactions was then performed. Throughout series G the products were analysed at a pressure fall of 20.0 torr. From the reaction analyses (table 6.7a), it can be seen that the butene distribution is similar to that observed over the catalysts treated with hydrogen sulphide in series A, C and F. The initial hydrogenation activities of these catalysts were compared after their sulphur treatment. The results from the first reaction after sulphur treatment reveals that catalyst G had a higher activity (9.0 torr/min., reaction $^{G}/1$) than catalyst A (5.0 torr/min., reaction $^{A}/6$) and catalyst F (3.0 torr/min., reaction $^{F}/6$); however it was lower than that observed over catalyst C (~19.0 torr/min., reaction $^{C}/1$). The butene distribution was independent of the number of reactions performed. The treated catalyst showed a gradual decrease in activity with reaction number. A similar reaction of thiophene with

hydrogen was carried out, for 40 minutes, and the catalyst was then evacuated at 350°C for 15 minutes. A further series of butadiene hydrogenation reactions was carried out after this treatment. The results illustrate that the butene distribution and the activity were similar to those observed after the first sulphur treatment, except that the activity achieved the steady state after fewer hydrogenation runs. The results for this series of reactions are given in table 6.7b.

An attempt was made to remove any sulphur deposited on the surface of the catalyst as a result of the reactions of thiophene with hydrogen. For this purpose the catalyst was placed in a furnace, in a flow of nitrogen for a period of one hour at room temperature. The temperature of the furnace was then raised gradually up to 750°C and maintained at this temperature for a further five hours. The catalyst was then cooled down gradually to room temperature but was kept under the flow of nitrogen for a further ten hours. A pale yellow sublimate presumed to be sulphur, was observed on the cooler parts of the tube. The catalyst was transferred to the reaction vessel and a series of butadiene hydrogenation reactions was carried out. The results illustrate that there was a marked change in the butene distribution and in the initial rate of reaction: the but-1-ene yield increased, relative to the trans-but-2-ene and the cis-but-2-ene yields. The initial rate of reaction was also at first increased as

the result of sulphur removal. The results are shown in table 6.7c.

Figure 6.11 shows the variation of the butene distribution and the activity with the number of reactions performed, and as a result of the various treatments. The broken lines drawn in the figure 6.11 represent the variation of the butene distribution and the initial rate of reaction over the fresh evacuated catalyst as deduced from earlier results in series A and B.

Table 6.7

The variation of the butene distribution and the initial rate of reaction over a sulphur treated catalyst via hydrodesulphurisation of thiophene (series G)

Table 6.7a After first hydrodesulphurisation reaction

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
	1-B	t-2-B	c-2-B			
G/1	30.6	49.8	19.6	2.54	0.44	9.00
G/2	30.3	48.4	21.3	2.27	0.43	6.50
G/3	28.7	49.5	21.8	2.27	0.40	6.00
G/4	30.3	49.9	19.8	2.52	0.43	4.50
G/5	29.9	48.5	21.6	2.24	0.43	4.50

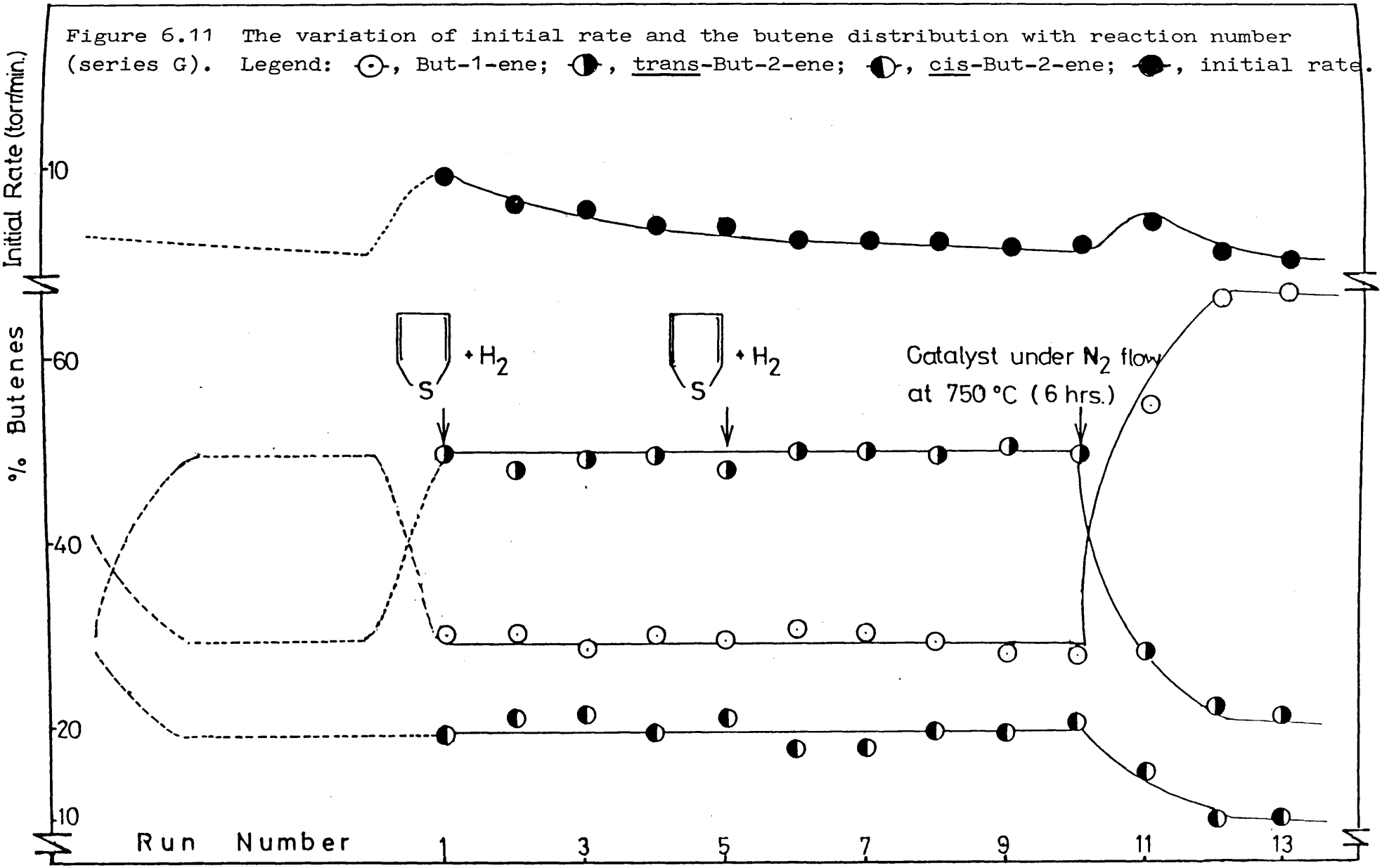
Table 6.7b After second hydrodesulphurisation reaction

Reaction	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
G/6	31.3	50.6	18.1	2.79	0.46	3.00
G/7	31.3	50.5	18.2	2.77	0.46	3.00
G/8	30.0	50.1	19.9	2.52	0.43	3.00
G/9	28.6	51.4	20.0	2.57	0.40	2.50
G/10	28.2	50.5	21.3	2.37	0.39	2.50

Table 6.7c

Reaction	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
G/11	55.5	28.6	15.9	1.80	1.25	5.00
G/12	67.2	23.0	9.8	2.35	2.05	2.00
G/13	67.4	21.7	10.9	1.99	2.07	0.50

Figure 6.11 The variation of initial rate and the butene distribution with reaction number (series G). Legend: ⊙, But-1-ene; ◑, trans-But-2-ene; ◐, cis-But-2-ene; ●, initial rate.



6.4 The variation of butene distribution with increasing extent of reaction

Three series of reactions were studied in which the following standard conditions were used. Butadiene hydrogenation at 350°C used a mixture of hydrogen and butadiene in the ratio 3:1 at an initial pressure of 200 torr, and the products were analysed after different pressure falls had been allowed to occur. Thiophene hydrodesulphurisation reactions were also carried out at 350°C, using a mixture of hydrogen and thiophene in the ratio 4:1, but no analysis of products was made.

Series H

A set of seven hydrodesulphurisation reactions of thiophene was carried out over a sample (1.00g) of catalyst, which had previously been used for butadiene hydrogenation reactions. A series of butadiene hydrogenation reactions was then carried out over the treated catalyst under the experimental conditions described above. The products were analysed after different pressure falls. The results shown in figure 6.12 (table 6.8) illustrate that the yield of but-1-ene decreases, while the yield of *cis*-but-2-ene increases with increasing pressure fall, whereas the percentage distribution of *trans*-but-2-ene was independent of the pressure fall.

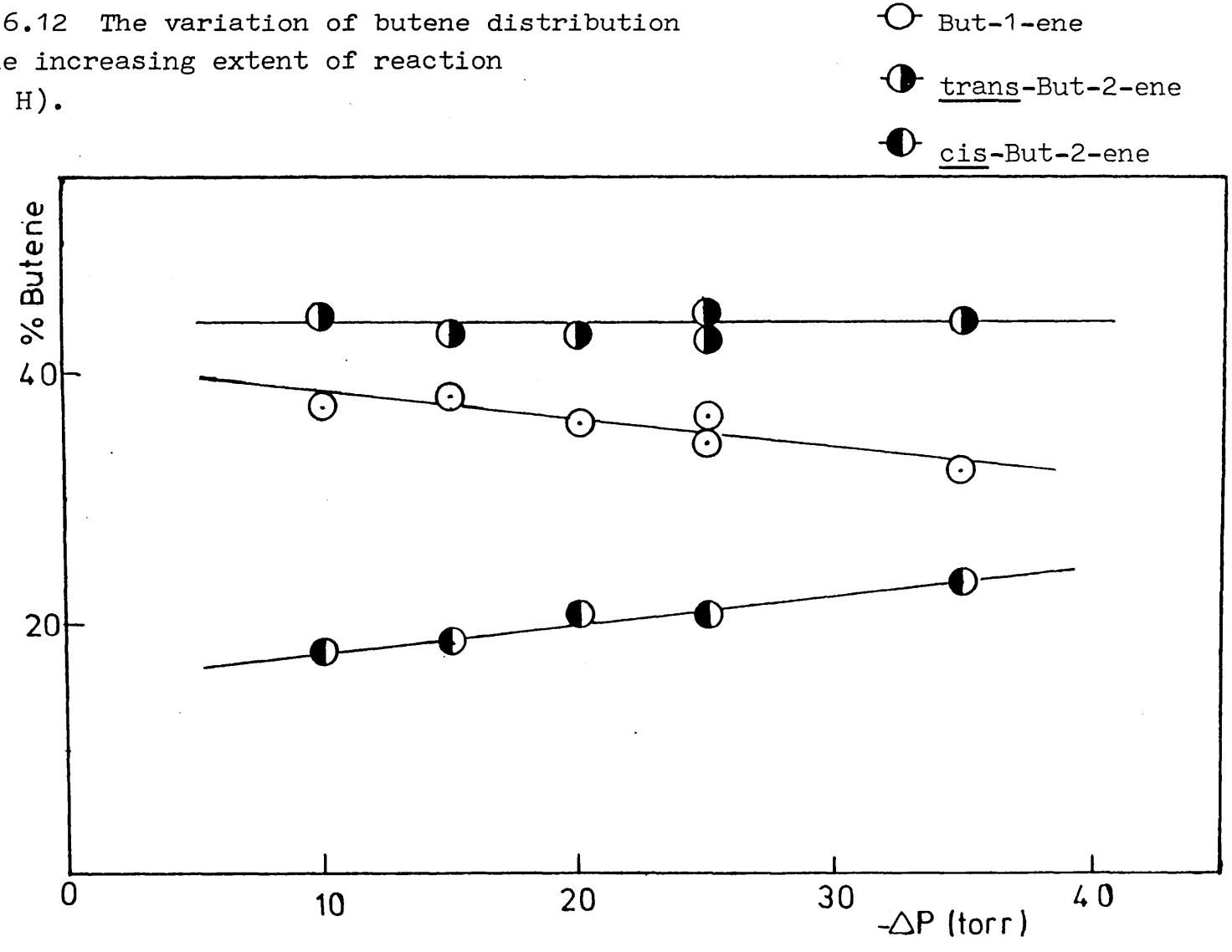
Table 6.8

Variation of the butene distribution with increasing pressure fall (series H)

Initial butadiene pressure = 50.0 ± 0.5 torr; initial hydrogen pressure = 150.0 ± 1.0 torr; temperature = 350°C; weight of the catalyst = 1.00g.

Reaction	$-\Delta P_{ext.}$ (torr)	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$
		1-B	t-2-B	c-2-B		
H/3	10.0	37.3	44.5	18.2	2.44	0.595
H/6	15.0	38.2	43.1	18.7	2.30	0.618
H/5	20.0	36.1	43.1	20.8	2.07	0.565
H/1	25.0	34.4	44.8	20.8	2.15	0.524
H/2	25.0	36.7	42.5	20.8	2.04	0.580
H/4	35.0	32.4	44.1	23.5	1.88	0.479

Figure 6.12 The variation of butene distribution with the increasing extent of reaction (series H).



Series I

A set of experiments was performed on a fresh 1.00g sample of catalyst as described for series J except that butadiene hydrogenation reactions were not carried out before the first treatment with hydrogen:thiophene mixture. The results are given in table 6.9 and figure 6.13 and reveal that the but-1-ene yield decreased, relative to the cis-but-2-ene yield increased with increasing extent of reaction. The percentage yield of the trans-but-2-ene was however independent of the extent of reaction.

Series J

Six consecutive hydrodesulphurisation reactions of thiophene were carried out over the catalyst used in series I. A further series of butadiene hydrogenation reactions were carried out and the products were analysed at various pressure falls. The results given in table 6.10 and figure 6.14 show that the variation of the butene distribution with increasing pressure fall was found to be similar to that found in series H and I reactions.

The important conclusion drawn from series H, I and J is that although the catalysts were pretreated under different conditions, yet the trend in butene distribution as a function of pressure fall was similar, that is, the but-1-ene yield decreased relative to the cis-but-2-ene yield increased with increasing pressure fall. There was no

relative change in the trans-but-2-ene yield with increasing extent of reactions.

Table 6.9

Weight of the catalyst = 1.00g

The variation of the butene distribution with increasing pressure fall (series I)

Reaction	$-\Delta P_{ext.}$ (torr)	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$
		1-B	t-2-B	c-2-B		
$^{I}/4$	10.0	35.4	50.7	13.9	3.65	0.548
$^{I}/6$	20.0	28.8	49.8	21.4	2.33	0.404
$^{I}/1$	25.0	28.0	48.7	23.3	2.09	0.389
$^{I}/2$	25.0	30.4	49.4	20.2	2.45	0.437
$^{I}/3$	25.0	30.4	52.4	17.2	3.05	0.437
$^{I}/7$	30.0	28.0	50.8	21.2	2.40	0.389
$^{I}/5$	40.0	24.9	49.0	26.1	1.88	0.332

Table 6.10

The variation of butene distribution with pressure fall (series J)

Reaction	$-\Delta P_{ext.}$ (torr)	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$
$^{J}/3$	10.0	33.4	46.7	19.9	2.35	0.502
$^{J}/6$	15.0	32.8	49.8	17.4	2.86	0.488
$^{J}/5$	20.0	34.4	49.0	16.6	2.95	0.524
$^{J}/1$	25.0	34.5	44.5	21.0	2.12	0.527
$^{J}/2$	25.0	28.2	46.9	24.9	1.88	0.393
$^{J}/4$	38.5	24.8	48.2	27.0	1.79	0.330

Figure 6.13 The variation of butene distribution with the increasing extent of reaction at 350°C (series I).

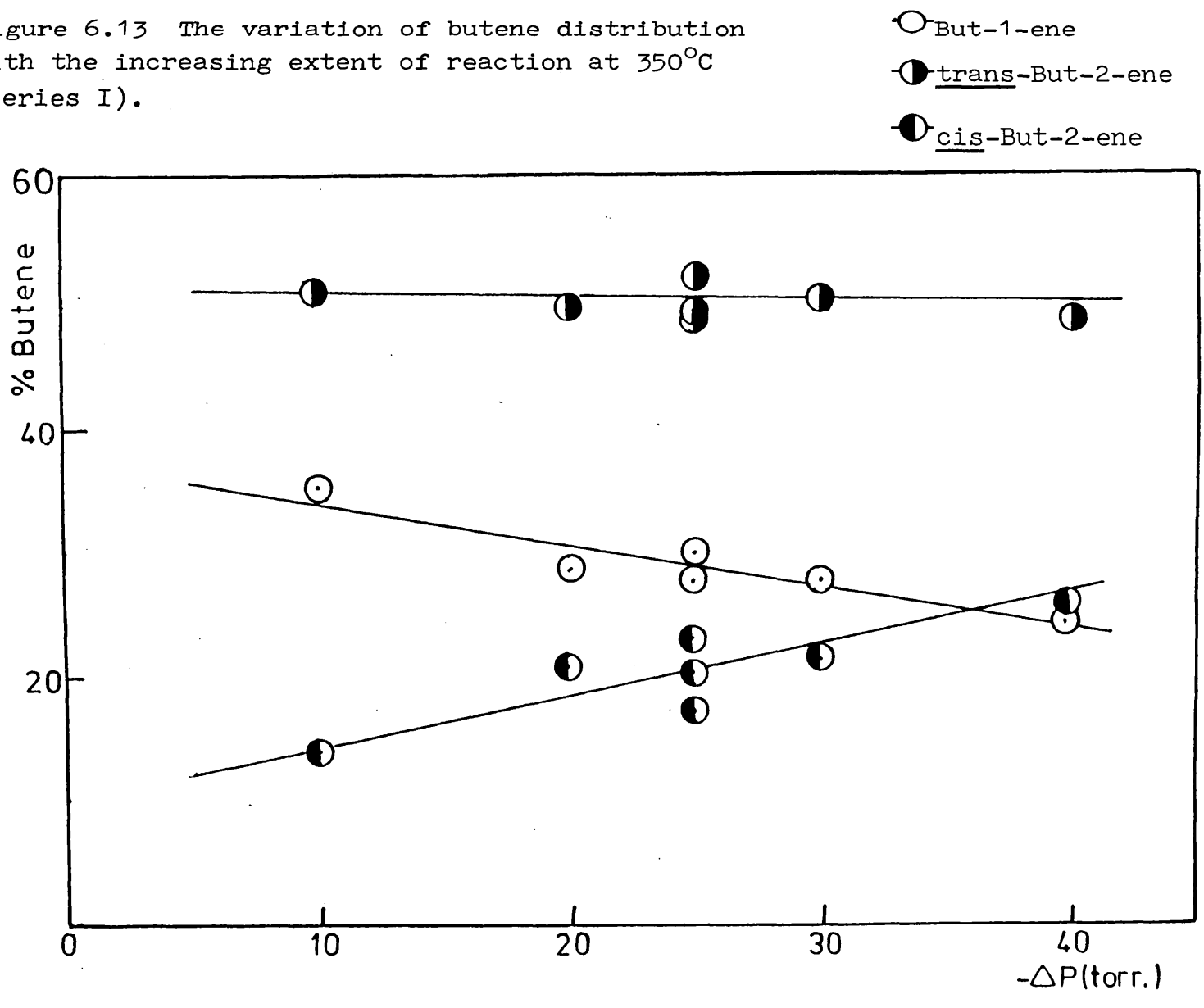
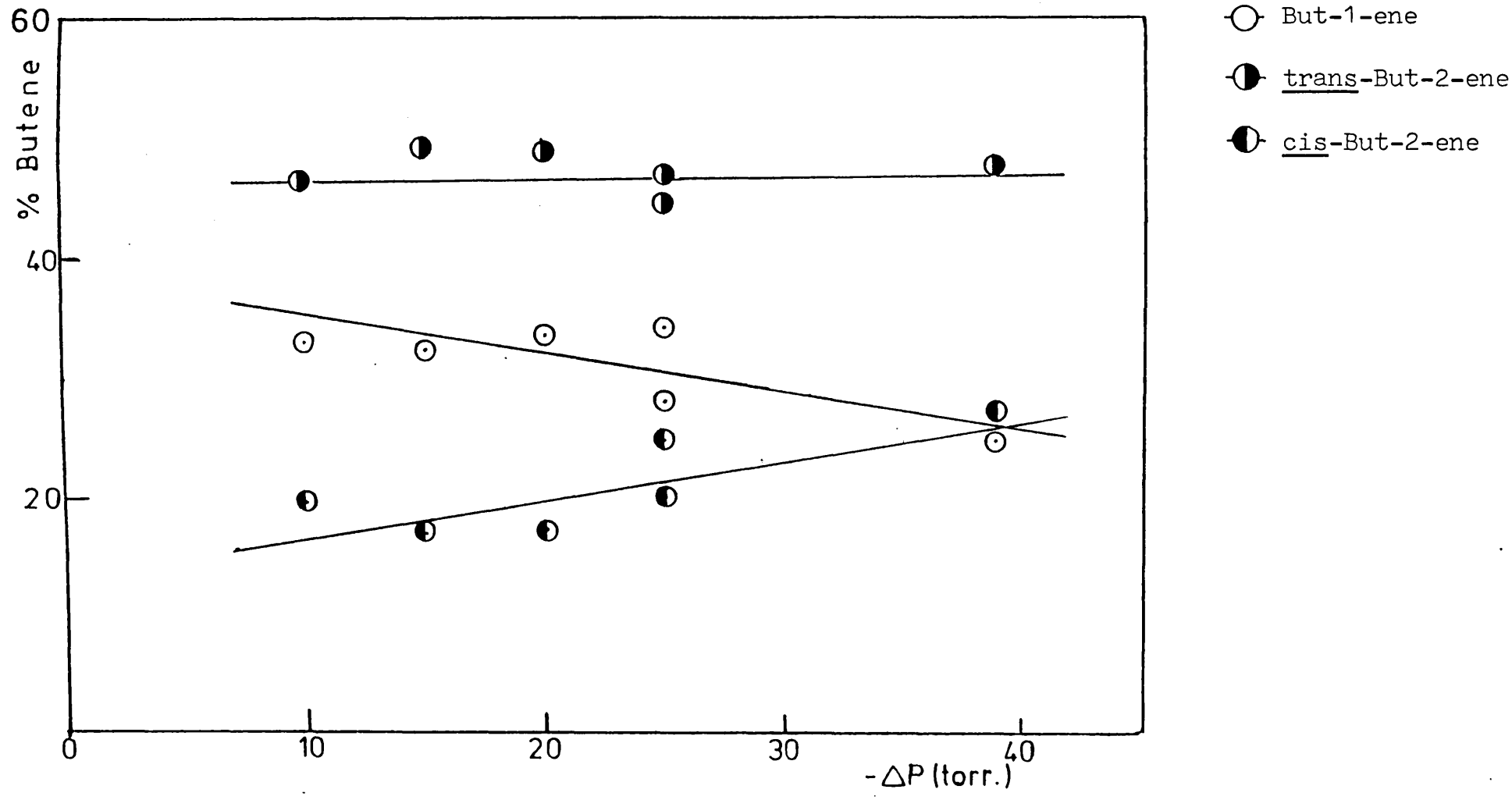


Figure 6.14 The variation of butene distribution as the function of pressure fall (series J).



6.5 The order with respect to hydrogen and effect of initial hydrogen pressure upon the butene distribution

A sample (1.00g) of catalyst which was used in section 6.4 series I and J was examined to determine the initial order with respect to hydrogen at 350°C in a series of reactions in which a constant butadiene pressure of 50.0 torr was used and the hydrogen pressure was varied between 80.0 torr and 250.0 torr. The results are shown in table 6.11.

The results are best illustrated by the $\frac{\text{trans}}{\text{cis}}$ ratio which shows that it decreased with increasing initial hydrogen pressure. The initial rate order with respect to hydrogen was found to be zero.

Table 6.11

Variation of the butene distribution with increasing hydrogen pressure

Initial butadiene pressure = 50.0 ± 1.0 torr; temperature = 350.0 ± 2.0°C; pressure fall at extraction = 15.0 ± 0.5 torr.

Reaction	P_{H_2} (torr)	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{\text{trans}}{\text{cis}})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
J/2	100.0	25.7	51.9	22.4	2.32	0.346	0.27
J/1	153.0	29.1	52.2	18.7	2.79	0.410	0.57
J/3	200.0	22.7	47.8	29.5	1.62	0.294	0.44
J/4	250.0	28.4	47.6	24.0	1.98	0.397	0.50

6.6 The order with respect to butadiene and the dependence of butene distribution upon initial butadiene pressure

In a series of experiments at 350°C, over a sample of catalyst used in section 6.5, the initial butadiene pressure was varied between 22.0 torr and 100.0 torr, and the hydrogen pressure was kept constant at 200.0 torr.

The initial rate was found to be independent of the butadiene pressure; this confirms that the order for butadiene is zero. The results are shown in table 6.12.

6.7 The dependence of butene distribution upon increasing temperature and the activation energy

The temperature was varied between 298°C and 401°C in a series of reactions using a hydrogen:butadiene ratio of 3:1. All the reactions were analysed after a pressure fall of 20.0 torr.

From the Arrhenius plot of $\log_{10}$ (initial rate) against $^1/T$ a value of 52.6 $\pm$ 1.0 KJ/mole was obtained for the activation energy (figure 6.15). The butene distribution showed a temperature dependence. From the results (table 6.13), it can be seen that the but-1-ene yield increases, whilst the trans-but-2-ene and cis-but-2-ene yields decrease with increasing temperature.

Table 6.12

Variation of the butene distribution with increasing butadiene pressure

Initial hydrogen pressure = 200.0 ± 2.0 torr; temperature = 350.0 ± 2.0°C

Reaction	P_{1-3B} (torr)	$-\Delta P_{ext.}$ (torr)	Butene distribution			$(\frac{trans}{cis})$	$\frac{1-B}{2-B}$	Initial rate (torr/min.)
			1-B	t-2-B	c-2-B			
K/1	22.0	5.0	31.9	45.3	22.8	1.99	0.468	0.28
K/2	50.0	10.0	24.3	48.9	26.8	1.82	0.321	0.50
K/3	75.0	5.5	32.1	46.8	21.0	2.23	0.473	0.45
K/4	100.0	5.0	29.3	51.9	18.8	2.75	0.414	0.50

Table 6.13

The variation of initial rate and the butene distribution with increasing temperature

Initial butadiene pressure = 50.0 ± 0.5 torr; initial hydrogen pressure = 150.0 ± 1.0 torr; pressure fall at extraction = 20.0 ± 0.5 torr.

Reaction	Temp. (°C)	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Initial rate (torr/min.)
		1-B	t-2-B	c-2-B			
$^{L}/4$	298	28.1	52.2	19.7	2.65	0.391	0.204
$^{L}/6$	324	26.0	51.3	22.7	2.26	0.351	0.25
$^{L}/3$	348	28.7	51.1	20.2	2.53	0.402	0.50
$^{L}/1$	347	29.4	48.7	21.9	2.22	0.416	1.50
$^{L}/5$	348	27.0	50.9	22.1	2.30	0.370	0.40
$^{L}/7$	378	30.6	50.5	18.9	2.67	0.441	0.666
$^{L}/2$	401	34.2	47.5	18.3	2.60	0.520	2.00

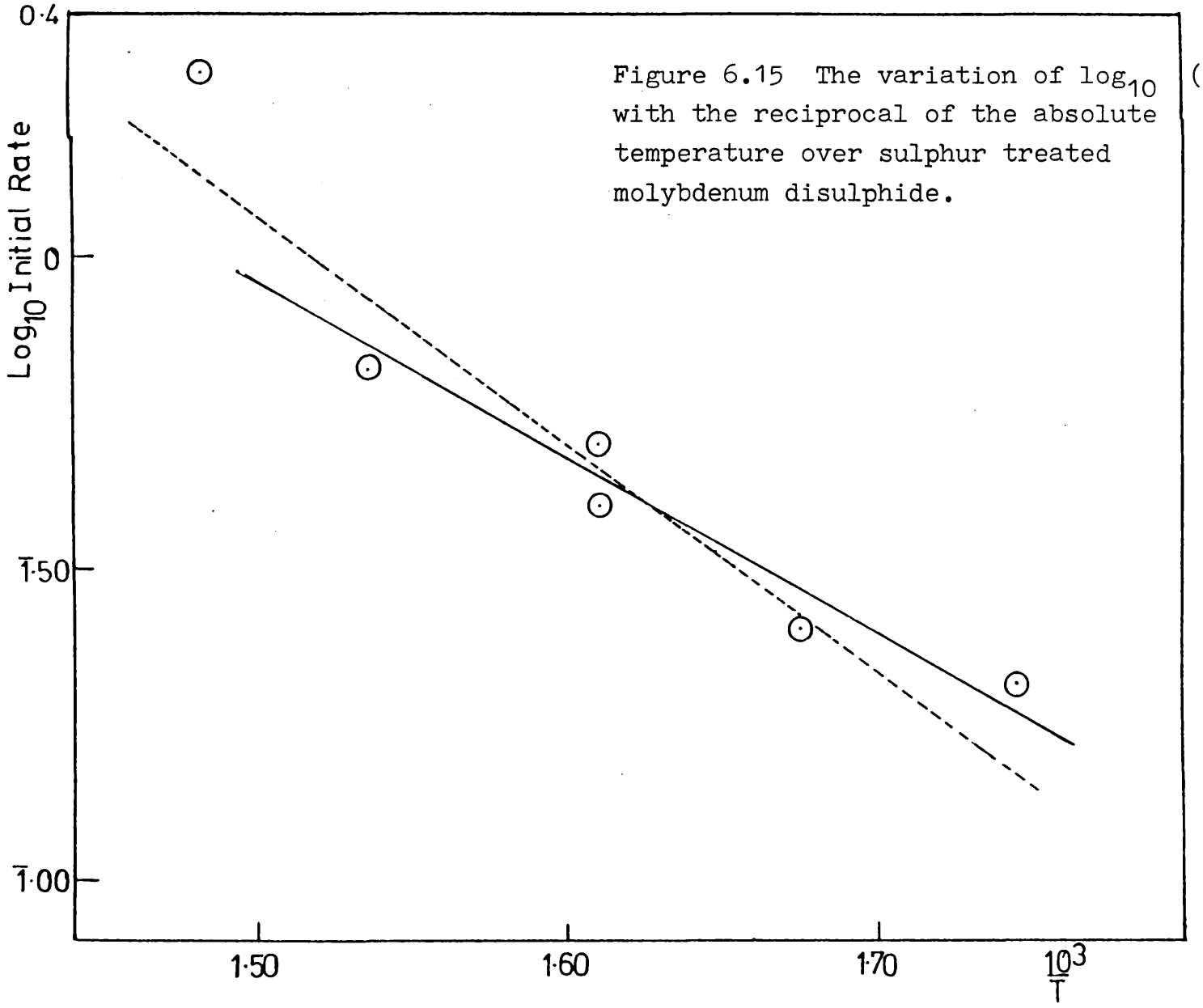


Figure 6.15 The variation of $\log_{10}$ (initial rate) with the reciprocal of the absolute temperature over sulphur treated molybdenum disulphide.

6.8 The variation of the butene distribution in the presence of hydrogen sulphide

A sample of catalyst (1.000g), which was previously used for butadiene hydrogenation and thiophene hydrodesulphurisation reactions was investigated for the possible interaction of butadiene with hydrogen sulphide (series M). The reactions of butadiene with hydrogen were then carried out (series N); and then another series of butadiene hydrogenation experiments was done in the presence of hydrogen sulphide (series O).

Series M

A series of three reactions of butadiene with hydrogen sulphide was carried out at 350°C using a butadiene:hydrogen sulphide ratio of approximately four. The products were extracted after a pressure fall of about 6.0 torr. The results show that hydrogen sulphide interacts with butadiene with the formation of all the three n-butenes which are found in almost their thermodynamic equilibrium composition. The results are given in table 6.14.

Table 6.14

Temperature = 350°C; initial butadiene pressure = 50 torr (approx.); initial hydrogen sulphide pressure = 12.0 torr (approx.); pressure fall at extraction = 6.0 torr (approx.).

Reaction	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$
	1-B	t-2-B	c-2-B		
M/1	18.6	50.5	30.9	1.63	0.229
M/2	18.2	56.6	25.2	2.25	0.222
M/3	16.2	57.9	25.9	2.24	0.193

Series N

A series of five butadiene hydrogenation reactions were carried out at 350°C using a butadiene:hydrogen ratio of 1:3. The products were extracted for analysis after different pressure falls. The results are given in table 6.15. It can be seen that the butene distribution is independent of the increasing pressure fall (figure 6.16).

Series O

Another series of butadiene hydrogenations was performed under similar experimental conditions to those used in series N but with added hydrogen sulphide ($\sim$6.0 torr). The reactions were analysed at various pressure falls. The results are shown in table 6.16 (broken lines shown in figure 6.16). It can be seen that the presence of hydrogen sulphide in the reaction did not significantly influence the butene distribution as compared with those observed in the reactions in the absence of hydrogen sulphide (series N).

Table 6.15

The variation of the butene distribution with increasing pressure fall in the absence of hydrogen sulphide (series N)

Initial butadiene pressure = 50.0 ± 0.5 torr; initial hydrogen pressure = 150.0 ± 1.0 torr; temperature = 350 ± 2.0°C

Reaction	$-\Delta P_{ext.}$ (torr)	Butene distribution 1-B	t-2-B	c-2-B	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$
N/1	10.0	-	-	-	-	-
N/2	10.0	38.5	43.3	18.2	2.38	0.626
N/4	15.0	38.6	44.6	16.8	2.65	0.629
N/3	25.0	37.2	44.2	18.6	2.38	0.592
N/5	35.0	37.5	42.9	19.6	2.19	0.600

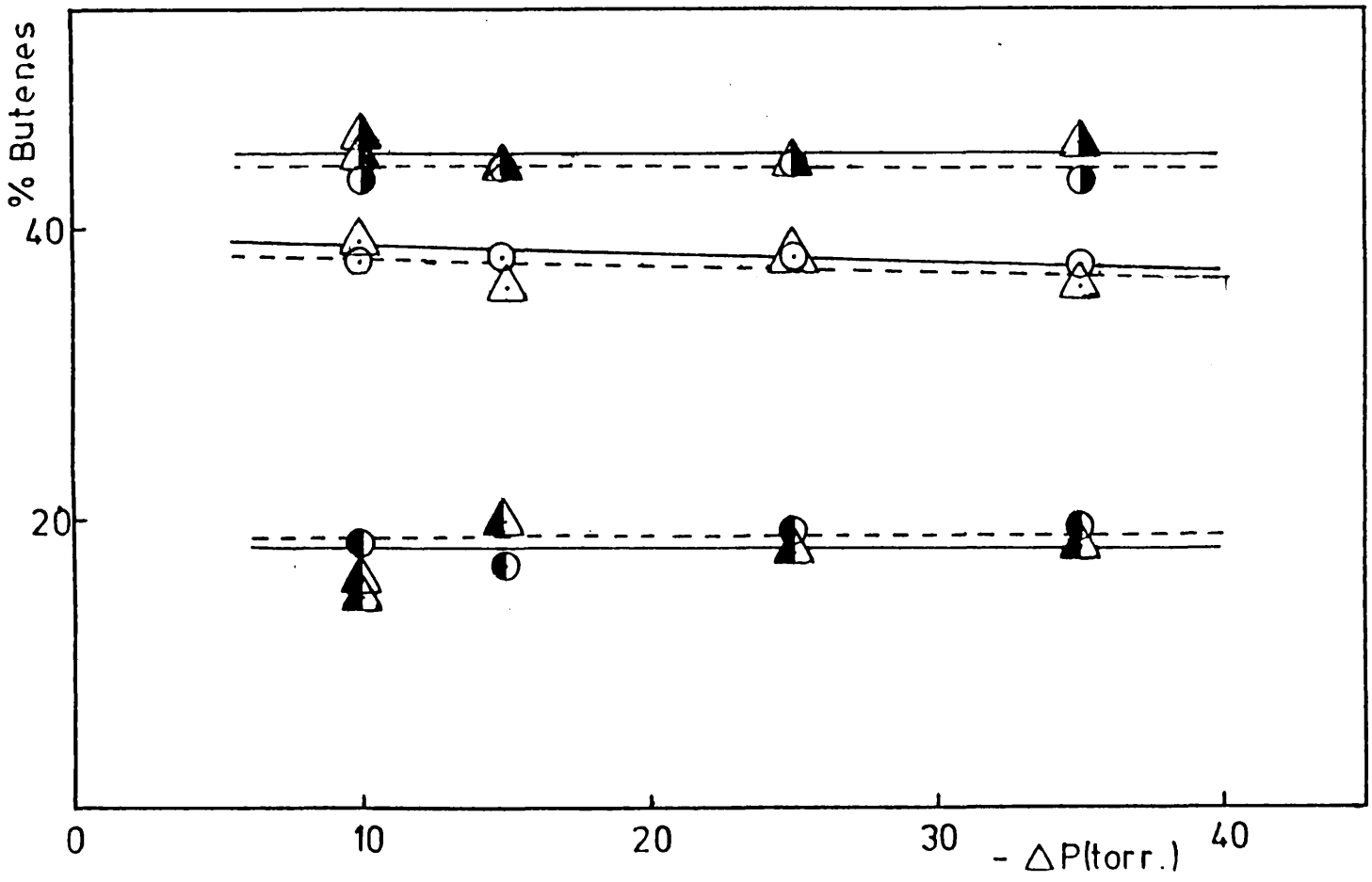
Table 6.16

The variation of the butene distribution with increasing pressure fall in the presence of hydrogen sulphide (series O)

The pressure of hydrogen sulphide in the reaction mixture = 6.0 torr (approx.).

Reaction	$-\Delta P_{ext.}$ (torr)	Butene distribution			$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$
		1-B	t-2-B	c-2-B		
O/1	10.0	39.1	45.1	15.8	2.85	0.642
O/5	10.0	39.1	46.5	14.4	3.23	0.642
O/3	15.0	35.8	44.0	20.2	2.18	0.558
O/2	25.0	37.9	44.4	17.7	2.51	0.610
O/4	35.0	39.1	46.5	14.4	3.23	0.642

Figure 6.16 The variation of butene distribution with increasing pressure fall, for series N and series O reactions.



Legend to figure 6.16

for series N

But-1-ene

trans-But-2-ene

cis-But-2-ene

for series O

But-1-ene

trans-But-2-ene

cis-But-2-ene

CHAPTER 7

7. THE REACTION OF THIOPHENE WITH HYDROGEN OVER MOLYBDENUM DISULPHIDE CATALYSTS

7.1 Introduction

Thiophene hydrodesulphurisation reactions were carried out over 1.00g samples of molybdenum disulphide catalysts. The reactions were usually carried out (unless otherwise specified) at 350°C using an initial thiophene pressure of 50.0 ± 1.0 torr and an initial hydrogen pressure of 200.0 ± 2.0 torr. The reactions were carried out by admitting thiophene to the catalyst, followed by hydrogen. The products were extracted at the required pressure fall. The reaction products were hydrogen sulphide, but-1-ene, *trans*-but-2-ene, *cis*-but-2-ene, *n*-butane and propane.

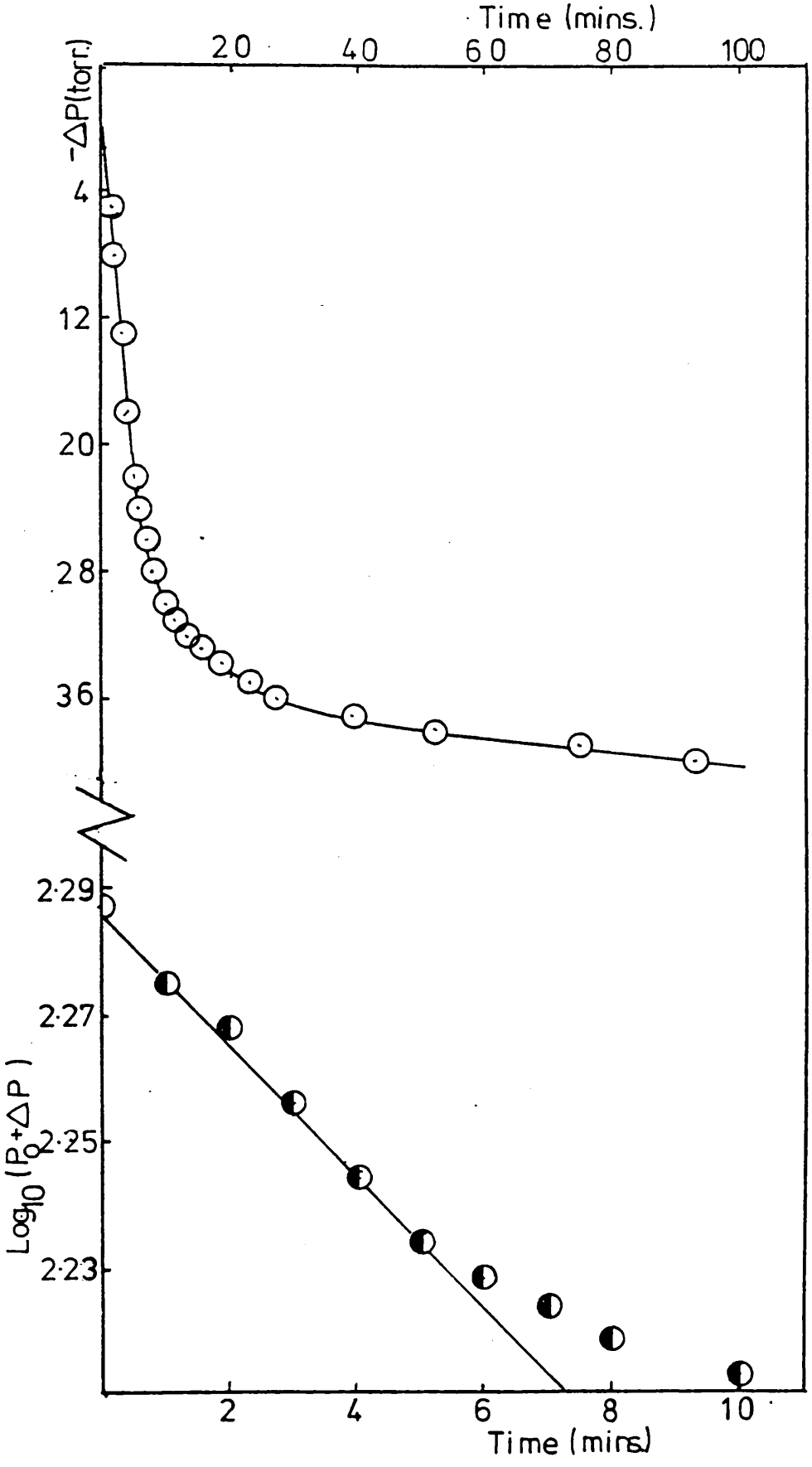
The term selectivity is defined as

$$\text{Selectivity} = \frac{\%\text{ yield of butene}}{\%\text{ yield of butene} + \%\text{ yield of } n\text{-butane}}$$

7.2 The pressure against time curves

Two samples of catalyst were tested to observe the change in pressure fall as a function of time. The pressure fall against time curves showed a continuous decrease in rate and were of the form shown in figures 7.1 and 7.2. Figure 7.1 shows a typical plot of pressure fall against time for a reaction over a fresh (1.00g) sample of catalyst. The reaction took place in two distinct stages. The first stage was fast

Figure 7.1 A typical pressure fall against time curve for the reaction of 50 torr thiophene with 200 torr of hydrogen at 350°C over untreated molybdenum disulphide. Also shown is the plot to test for first order.



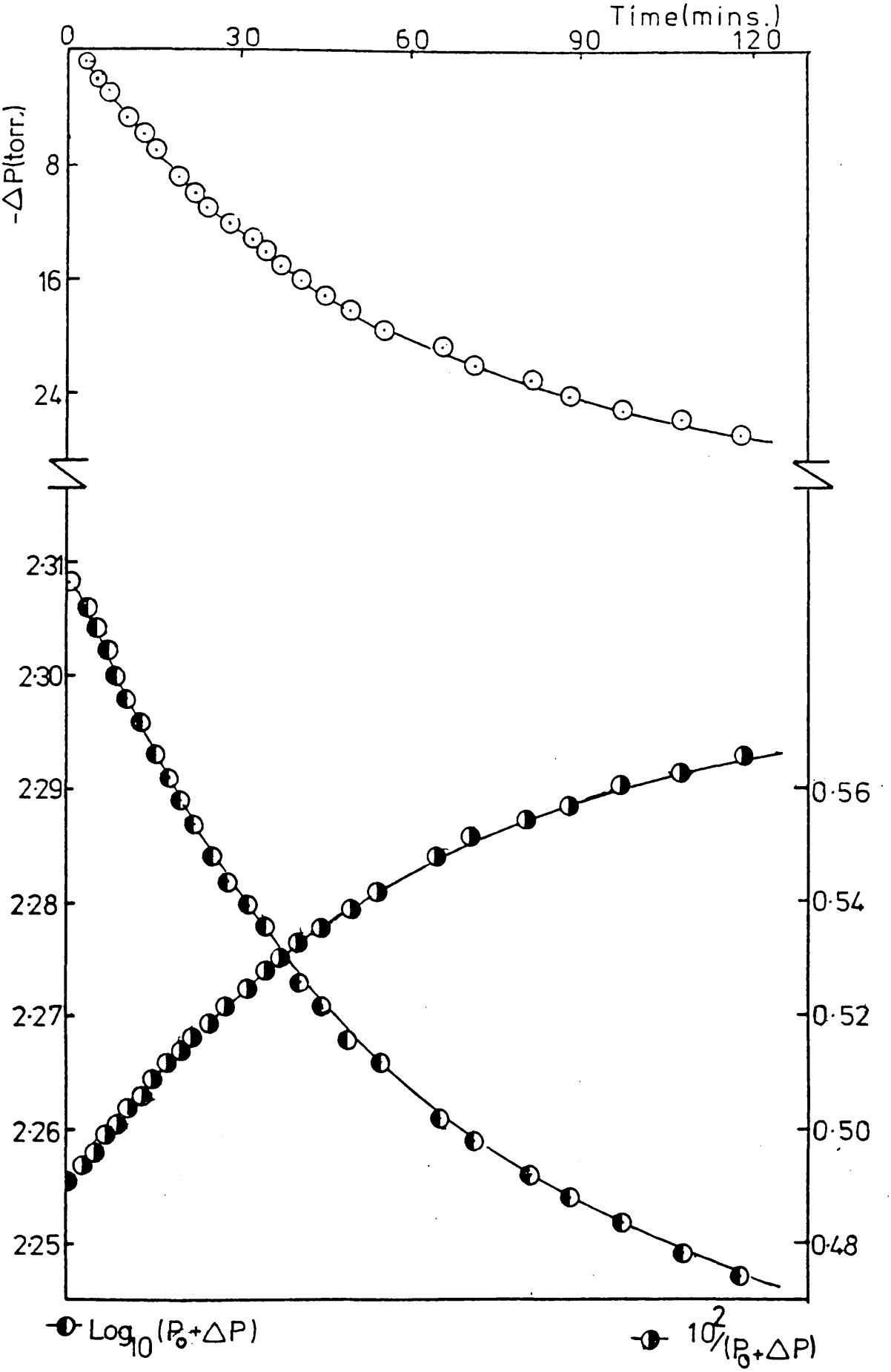


Figure 7.2 A typical pressure fall against time curve for the reaction of 50 torr of thiophene with 200 torr of hydrogen at 350°C over a 'used' catalyst. Also shown are the plots to test for first and second order.

compared with the second stage, where an abrupt decrease in the rate of pressure fall was observed. Also shown in figure 7.1 is the first order test plot derived from the first stage of the reaction. A typical pressure fall curve over a 0.50g sample of catalyst which had been previously used for hydrodesulphurisation reactions is shown in figure 7.2 along with plots to test for first and second order.

A series of thiophene hydrodesulphurisation reactions was carried out over a fresh (1.00g) sample of catalyst to investigate whether the rate changed with increasing use of the catalyst over several runs. The pressure fall against time curves for this series of reactions is shown in figure 7.3.

7.3 The effect of reaction number on the initial rate of reaction and on the product distribution

A series of thiophene hydrodesulphurisation reactions was carried out over a fresh (1.00g) sample of catalyst at 350^{o}C and the products were extracted for analysis at a fixed pressure fall of 20.0 $\pm$ 0.5 torr. The variations in initial rate of reaction, selectivity, and the product distribution with reaction number are given in table 7.1. The variation in the butene distribution with reaction number is illustrated by the trans:cis ratio and the but-1-ene:but-2-ene ratio. The latter was almost constant from one reaction to another, except in the case of reaction $^{A}/2$ which had a

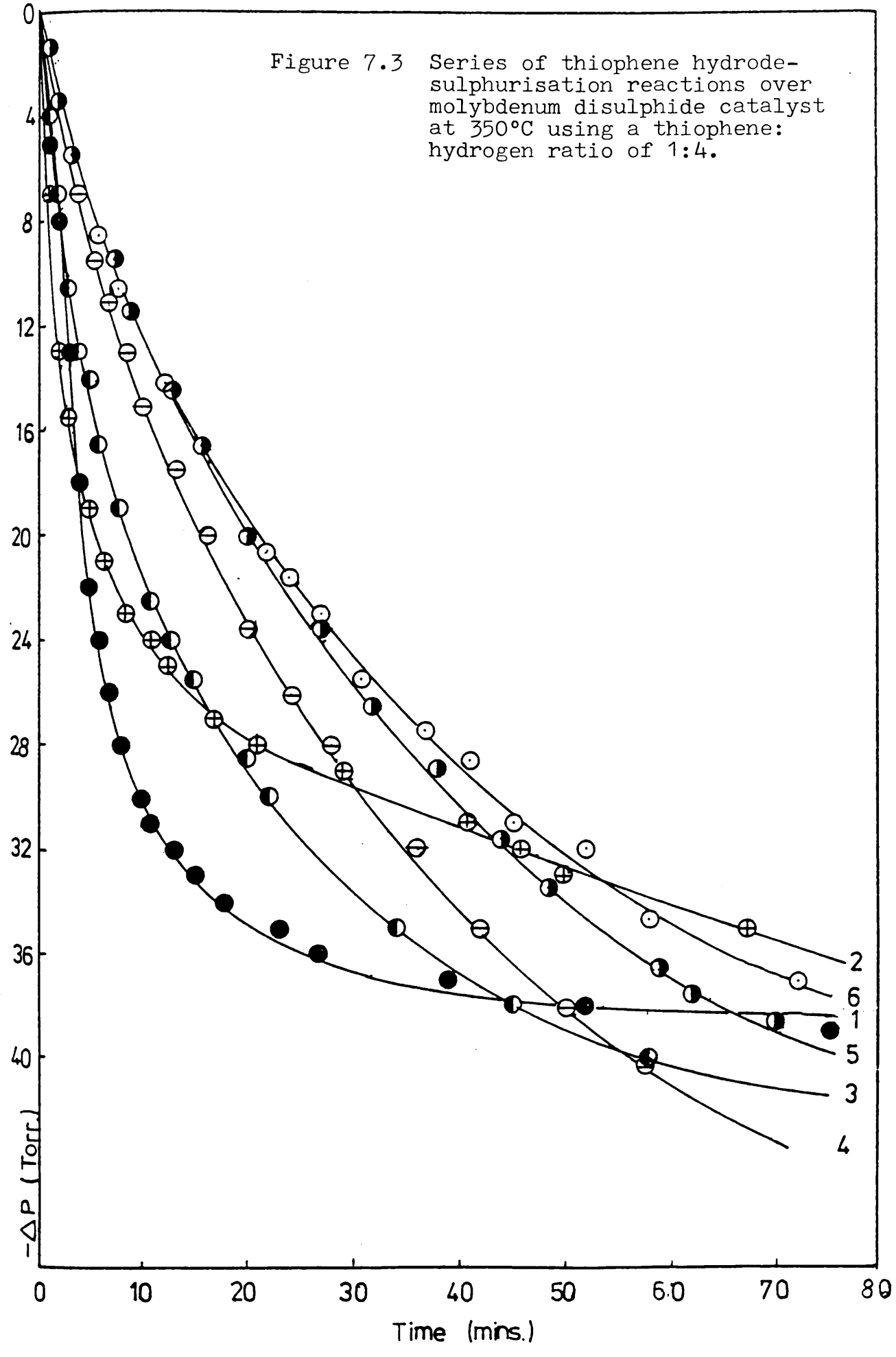


Figure 7.3 Series of thiophene hydrodesulphurisation reactions over molybdenum disulphide catalyst at 350°C using a thiophene: hydrogen ratio of 1:4.

Table 7.1

Dependence of initial rate, selectivity and product distribution upon reaction number

Initial thiophene pressure = 50.0 ± 1.0 torr; initial hydrogen pressure = 200.0 ± 2.0 torr; temperature = 350.0 ± 2.0°C; pressure fall at extraction = 20.0 ± 0.5 torr.

Reaction	Total product distribution (%)								Selectivity	Initial rate (torr/min.)
	Pr	n-B	1-B	t-2-B	c-2-B	H_2S	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$		
A/1	36.9	4.1	13.3	26.6	19.1	0.0	1.39	0.291	0.935	3.60
A/2	60.8	1.2	8.1	14.6	8.9	6.4	1.64	0.345	0.963	4.50
A/3	-	-	-	-	-	-	-	-	-	4.00
A/4	14.9	3.1	9.2	22.8	12.4	37.6	1.84	0.261	0.935	4.00
A/5	8.9	3.4	9.0	22.5	12.3	43.9	1.83	0.260	0.928	5.50
A/6	5.4	4.9	8.9	22.2	12.0	46.6	1.85	0.260	0.898	2.00
A/7	3.3	4.9	9.1	22.8	13.3	46.6	1.71	0.252	0.902	2.00
A/8	13.0	1.7	10.0	22.3	16.0	37.0	1.39	0.261	0.966	3.22

higher ratio. An interesting feature to emerge from the analysis of the reaction products was that in the first reaction of thiophene with hydrogen over the fresh sample of catalyst, no hydrogen sulphide was obtained in the product analysis, whereas in each of the subsequent reactions hydrogen sulphide was present in the reaction mixture.

7.4 The dependence of selectivity and product distribution upon pressure fall

Two samples of catalysts (A and B each weighing 1.00g) were used in this study. Both of these samples had been pretreated in different ways to determine the effects of the pretreatment upon the selectivity and the product distribution. The reactions were performed at 350°C, using a thiophene: hydrogen ratio of 1:4 and the products were analysed after various pressure falls.

Reactions over catalyst A

A series of six thiophene hydrodesulphurisation reactions (series B) was carried out over catalyst A which had been used previously for butadiene hydrogenation reactions at 350°C, using a hydrogen:butadiene ratio of 3:1. The reactions of thiophene with hydrogen were then carried out under similar conditions to those described above. From the results (table 7.2) it can be seen that the selectivity decreased with increasing pressure fall. The percentage yield of but-1-ene decreased relative to the cis-but-2-ene yield which increased,

Table 7.2

Dependence of selectivity and product distribution upon pressure fall (series B) on catalyst (A)

Reaction	$-\Delta P_{ext.}$ (torr)	Total product distribution (%) Pr	n-B	1-B	t-2-B	c-2-B	H_2S	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Selectivity
$^B/_1$	15.0	64.0	1.2	8.5	17.0	9.3	0.0	1.83	0.323	0.966
$^B/_3$	20.0	2.0	2.9	13.3	27.1	17.0	37.7	1.59	0.302	0.952
$^B/_5$	25.0	3.2	4.2	10.4	22.7	14.6	44.9	1.55	0.279	0.919
$^B/_6$	27.5	4.2	7.3	8.9	19.1	12.1	48.4	1.58	0.285	0.846
$^B/_2$	30.0	4.9	4.7	17.8	34.5	23.0	15.1	1.50	0.310	0.941
$^B/_4$	40.0	0.0	6.8	9.3	21.3	13.7	48.9	1.55	0.266	0.867

Table 7.3

The variation of selectivity and product distribution with pressure fall (series C) on catalyst (A)

Reaction	$-\Delta P_{ext.}$ (torr)	Total product distribution (%) Pr	n-B	1-B	t-2-B	c-2-B	H_2S	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Selectivity
C/1	15.0	63.8	0.7	9.6	16.2	9.7	0.0	1.67	0.371	0.981
C/3	20.0	15.0	4.3	10.5	22.0	13.5	34.7	1.63	0.296	0.915
C/5	25.0	13.6	3.7	11.5	26.3	15.9	29.0	1.65	0.273	0.936
C/2	30.0	13.5	6.0	15.2	32.9	21.5	10.0	1.53	0.279	0.920
C/4	40.0	9.0	12.2	6.6	18.2	11.4	42.6	1.60	0.223	0.748

however no significant change was observed in the relative yield of the trans-but-2-ene with increasing pressure fall (figure 7.4).

This catalyst (A) was again used for butadiene hydrogenation reactions, followed by another series of thiophene hydrodesulphurisation reactions (series C). The results are given in table 7.3. The variations in butene distribution and selectivity are shown in figure 7.5, from which it can be seen that the trends in the butene distribution and in the selectivity as a function of pressure fall are similar to those found in series B (figure 7.4).

Reactions over catalyst (B)

A fresh (1.00g) sample of catalyst (B) was pretreated by carrying out a series of eight thiophene hydrodesulphurisation reactions under similar experimental conditions to those described above. The products were analysed after a pressure fall of 20.0 $\pm$ 0.5 torr. The reaction analyses obtained from the series are those (table 7.1) given in section 7.3. A further series of hydrodesulphurisation reactions was performed over the pretreated catalyst (B); the products were extracted for analysis at various pressure falls (series D). The variation in total product distribution and selectivity is listed in table 7.4, whilst figure 7.6 shows the variation in butene distribution and selectivity with pressure fall. The variation of C_4-hydrocarbon and hydrogen sulphide distributions

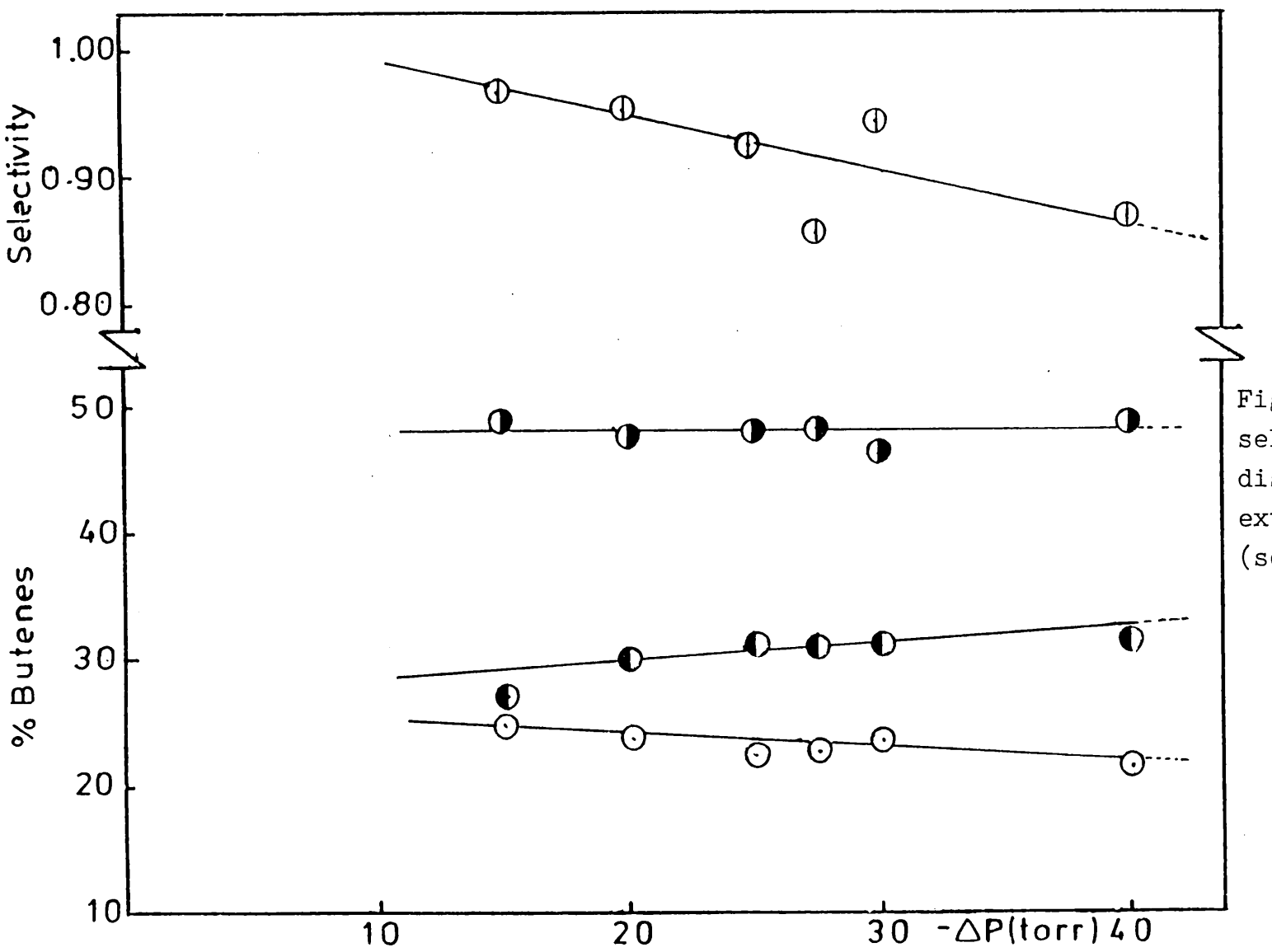


Figure 7.4 The variation of selectivity and the butene distribution with increasing extent of reaction at 350°C (series B).

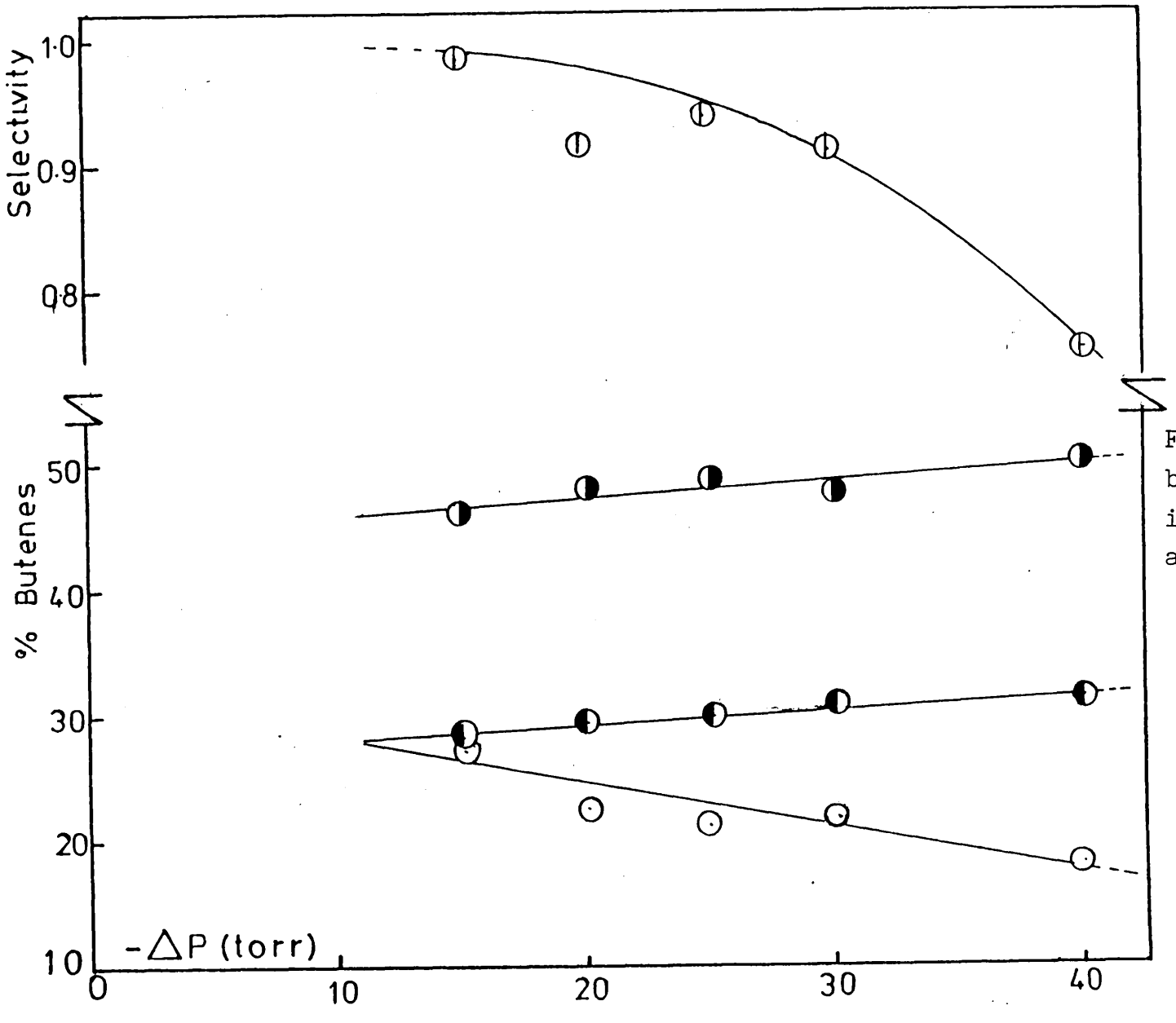


Figure 7.5 The variation of butene distribution with increasing extent of reaction at 350°C (series C).

Table 7.4

The variation of selectivity and product distribution with pressure fall (series D) over catalyst (B)

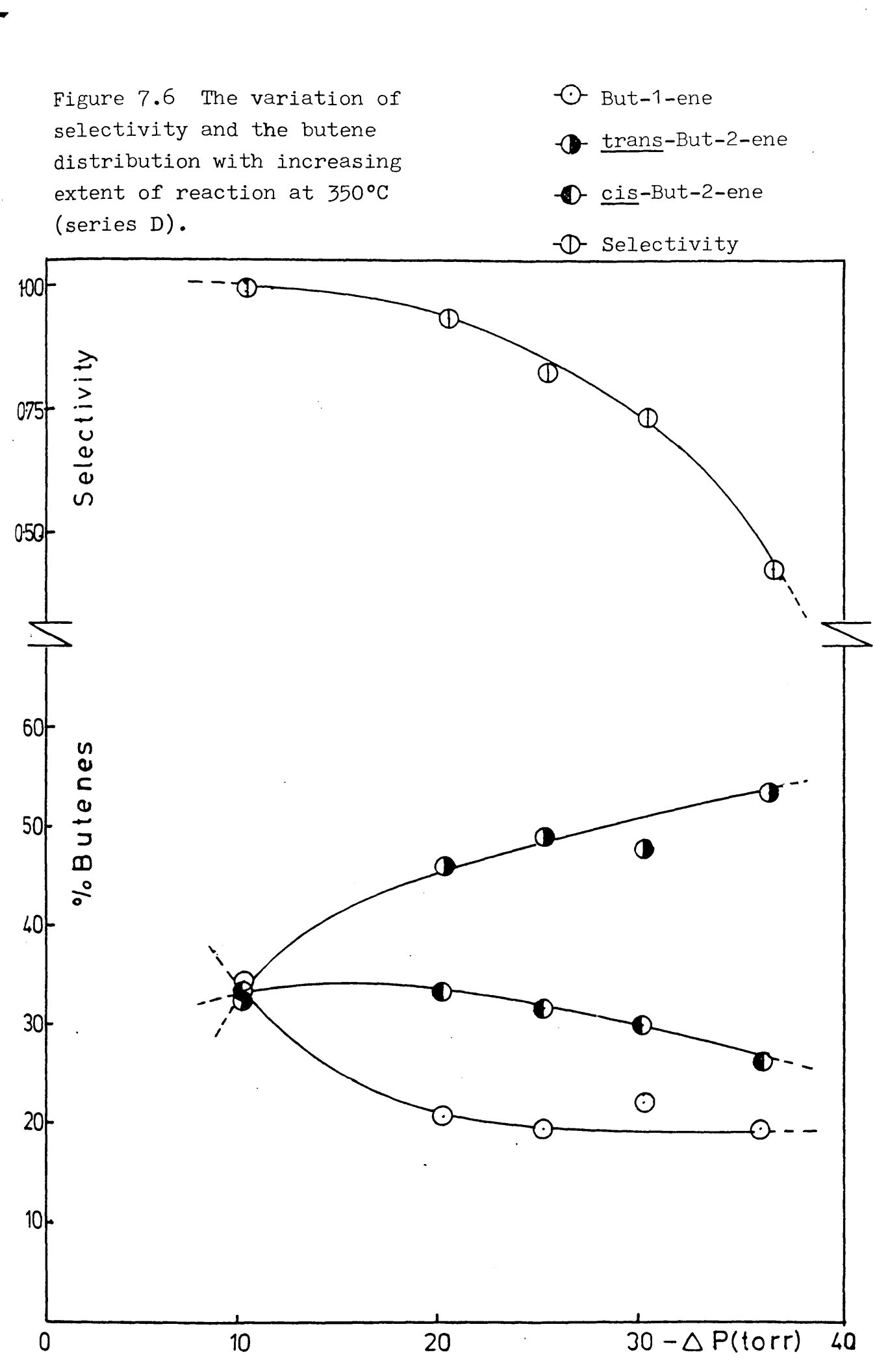
Reaction	$-\Delta P_{ext.}$ (torr)	Total product distribution (%) Pr	n-B	1-B	t-2-B	c-2-B	H_2S	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Selectivity
D/4	10.0	66.3	0.0	4.5	4.2	4.3	20.7	0.977	0.529	1.000
D/1	20.0	13.0	1.7	10.0	22.3	16.3	37.0	1.39	0.261	0.966
D/3	25.0	3.8	8.0	7.1	18.1	11.8	51.3	1.53	0.237	0.822
D/5	30.0	7.2	11.1	6.8	14.6	9,2	51.1	1.59	0.286	0.734
D/2	36.0	11.2	22.5	3.4	9.2	4.5	49.2	2.04	0.248	0.432

Table 7.5

Dependence of selectivity and product distribution upon increasing pressure fall (series E) over catalyst (B)

Reaction	$-\Delta P_{ext.}$ (torr)	Total product distribution (%) Pr	n-B	1-B	t-2-B	c-2-B	H_2S	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Selectivity
E/5	10.0	4.7	0.6	4.6	8.1	5.0	36.0	1.62	0.351	0.967
E/3	20.0	17.4	1.5	7.2	17.1	9.9	46.9	1.73	0.267	0.958
E/1	20.0	22.2	4.0	7.2	17.5	11.2	37.9	1.56	0.251	0.900
E/2	20.0	15.8	2.4	6.8	17.2	11.4	46.4	1.51	0.238	0.937
E/7	25.0	5.6	5.8	7.2	17.4	11.7	52.3	1.49	0.247	0.862
E/6	30.0	5.0	7.8	6.8	16.6	10.8	53.0	1.54	0.248	0.814
E/4	35.5	5.6	16.7	4.5	10.7	5.8	56.7	1.84	0.273	0.557

Figure 7.6 The variation of selectivity and the butene distribution with increasing extent of reaction at 350°C (series D).



as a function of pressure fall is shown graphically in figure 7.7.

The catalyst was then used for butadiene hydrogenation reactions, followed by another series of thiophene hydrodesulphurisation reactions (series E); the products were analysed at various pressure falls. The results are listed in table 7.5. Figure 7.8 illustrates the variation of butene distribution as a function of pressure fall, whilst the variation of C_4-hydrocarbon and hydrogen sulphide percentage composition is shown in figure 7.9. Comparing figure 7.7 and figure 7.9, it is apparent that the trend in the product distribution was similar in both the series (D and E) of reactions. From these results (tables 7.4 and 7.5), it can be seen that the selectivity decreased as the pressure fall increased.

7.5 The initial rate order with respect to hydrogen and the variation of selectivity and product distribution with initial pressure

In a series of experiments at 350^{o}C, the hydrogen pressure was varied between 102.5 torr and 285.0 torr and the thiophene pressure was kept constant at 50.0 torr. The reaction products were extracted for analysis after a pressure fall of 15.0 $\pm$ 0.5 torr. The results are shown in table 7.6.

From the results it can be seen that increasing the hydrogen pressure had no significant effect upon the butene

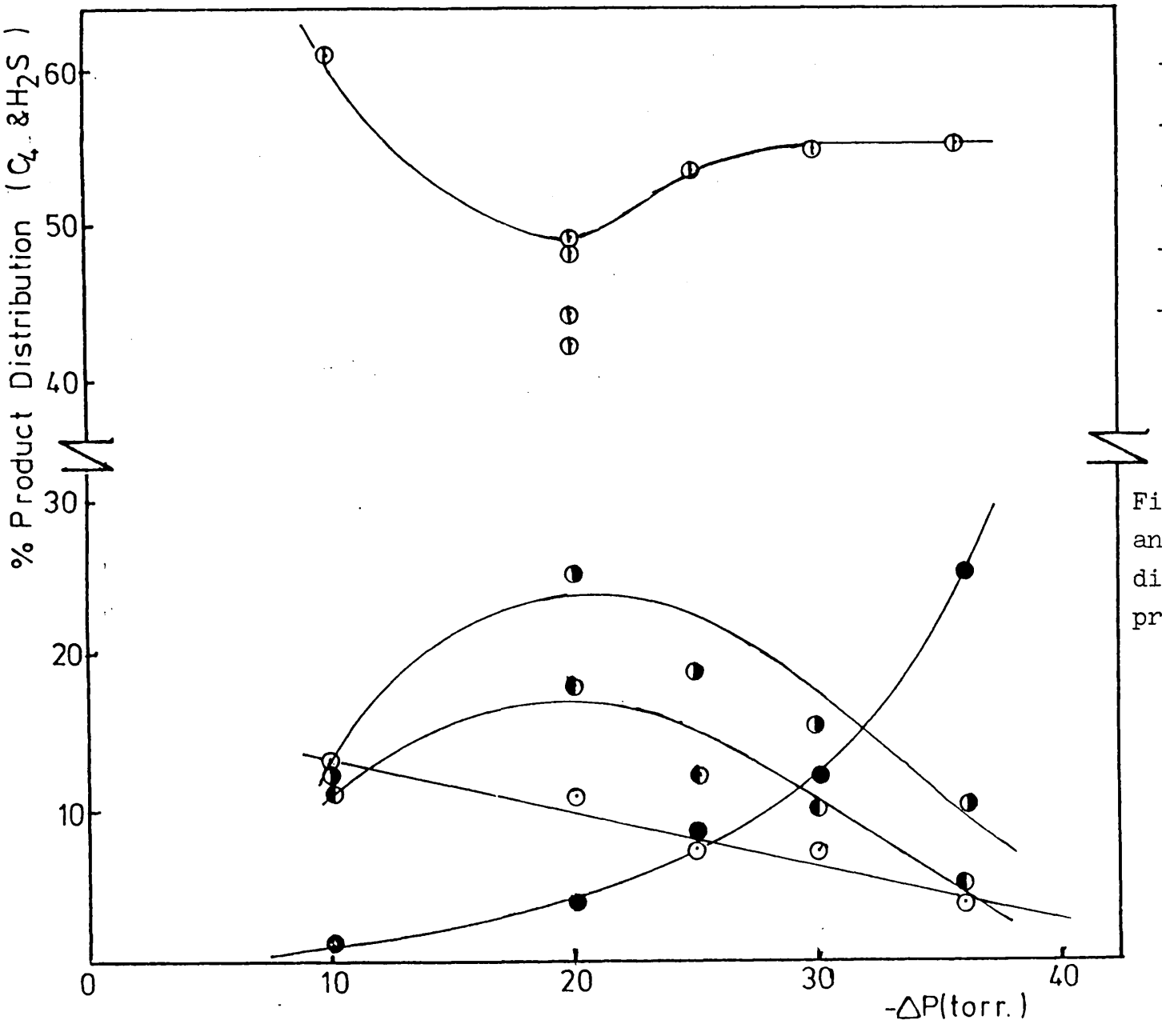
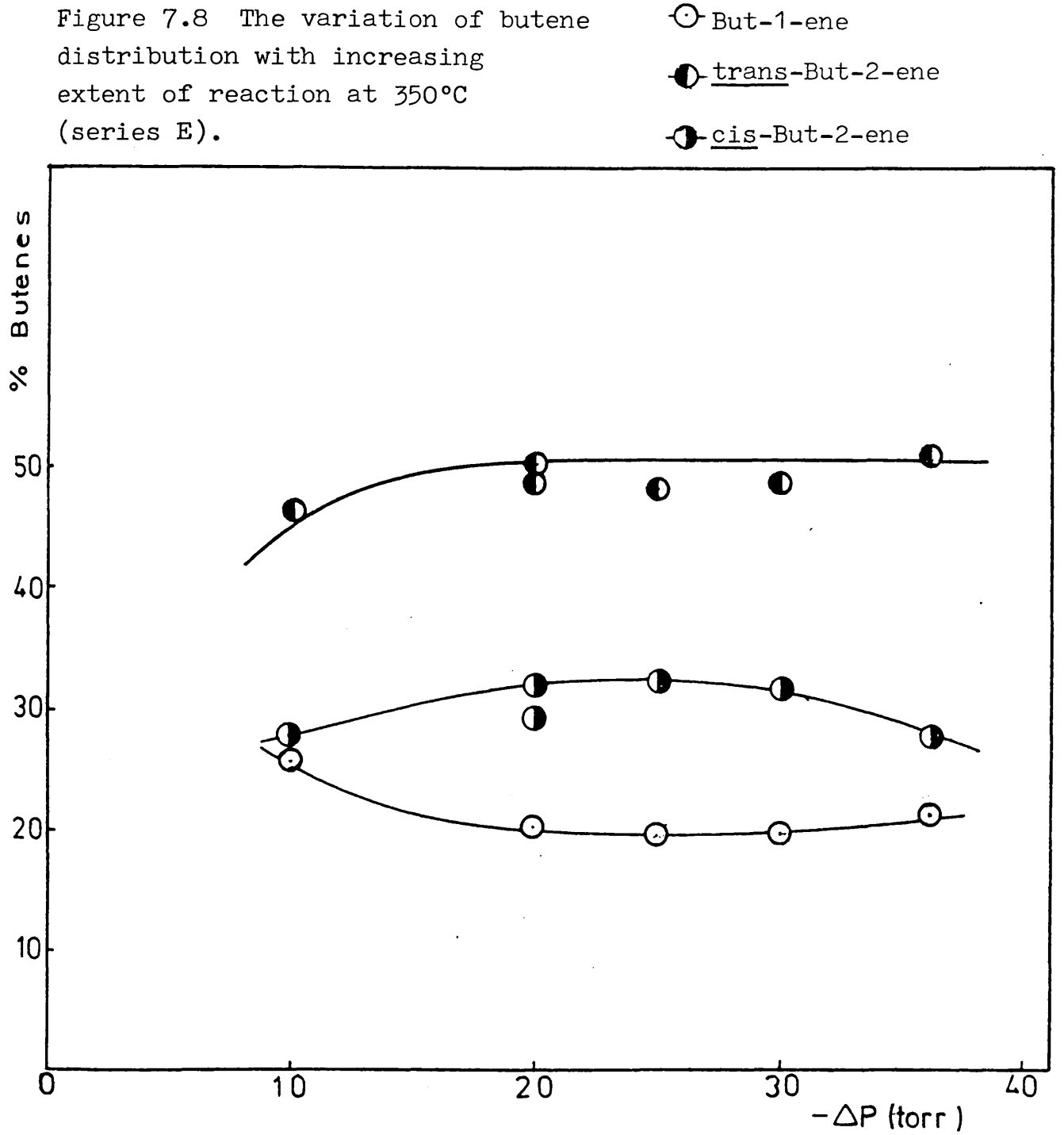


Figure 7.7 The variation of C_4 and hydrogen sulphide product distribution as the function of pressure fall (series D).

Figure 7.8 The variation of butene distribution with increasing extent of reaction at 350°C (series E).



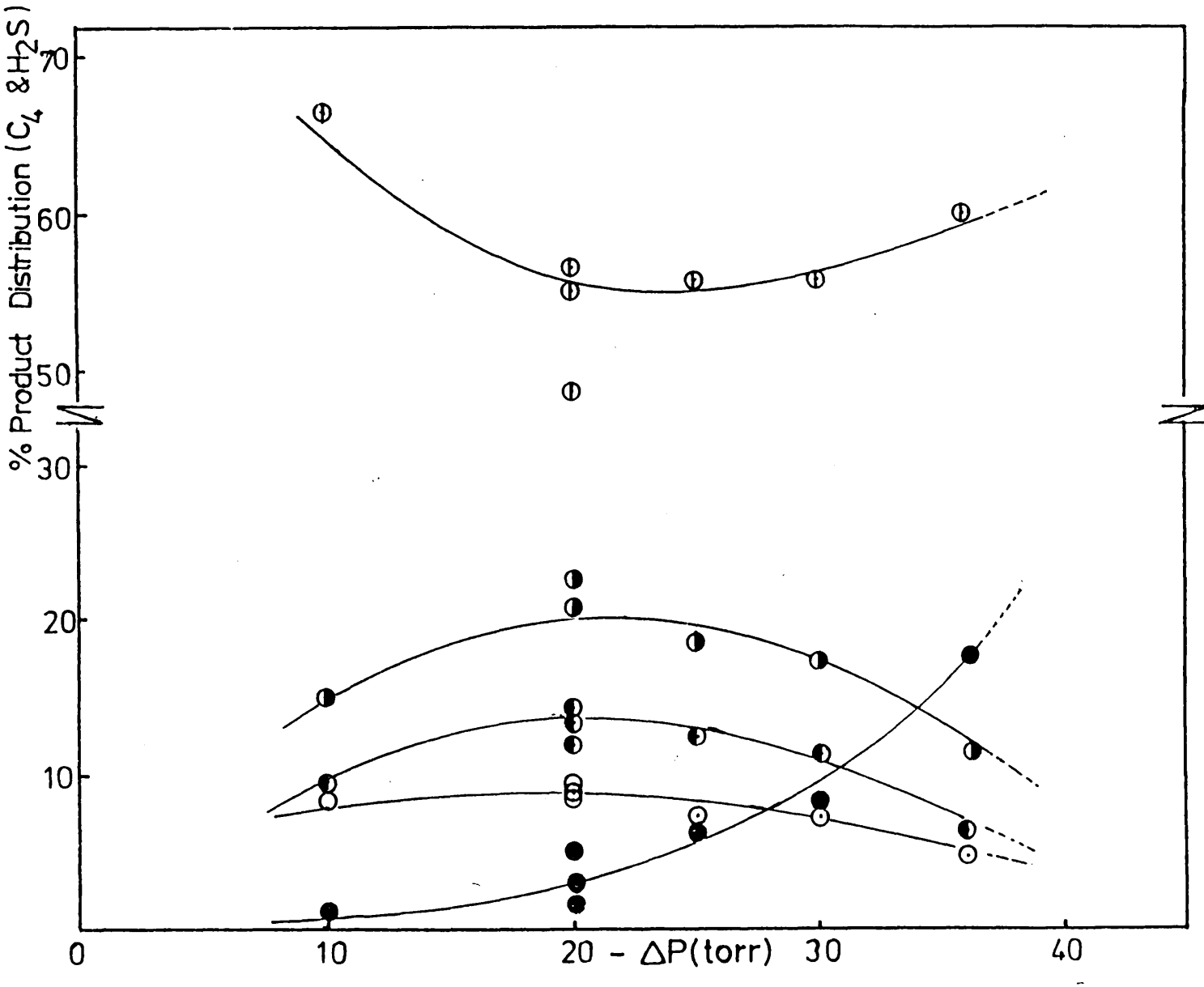


Figure 7.9 The variation of C_4-hydrocarbon and hydrogen sulphide percentage composition with increasing extent of reaction (series E).

Table 7.6

Dependence of initial rate, selectivity and product distribution upon initial hydrogen pressure

Initial thiophene pressure = 50.0 ± 1.0 torr; pressure fall at extraction = 15.0 + 0.5 torr; temperature = 350.0 ± 2.0°C

Reaction	P_{H_2} (torr)	Total product distribution (%) Pr	n-B	1-B	t-2-B	c-2-B	H_2S	$(\frac{trans}{cis})$	$\frac{1\text{-B}}{2\text{-B}}$	Selectivity	Initial rate (torr/min)
F/2	102.5	5.1	2.3	9.4	19.9	10.9	52.4	1.83	0.305	0.946	0.75
F/1	194.0	11.8	2.4	9.3	19.1	11.0	46.4	1.74	0.309	0.943	3.00
F/5	208.0	2.5	2.8	10.0	21.4	12.5	50.7	1.71	0.295	0.940	1.00
F/4	250.0	2.9	3.6	9.8	20.6	11.4	51.7	1.81	0.306	0.921	0.80
F/3	285.0	2.9	4.4	9.1	20.3	12.1	51.2	1.68	0.281	0.904	0.83

distribution. The selectivity decreases with increasing hydrogen pressure, (figure 7.10). No initial rate order could be determined since the activity varied considerably from reaction to reaction.

7.6 The order with respect to thiophene and the dependence of initial rate, selectivity and product distribution upon initial thiophene pressure

In a series of reactions at 350°C, the initial thiophene pressure was varied between 20.0 and 61.0 torr at a constant hydrogen pressure of 200.0 torr. The results given in table 7.7 show that the selectivity first increased and then decreased with increasing initial pressure of thiophene. There was a non linear increase in the initial rate of reaction with increasing initial pressure of thiophene (figure 7.11). The butene distribution showed a thiophene pressure dependence which is best illustrated by the trans:cis ratio and the but-1-ene:but-2-ene ratio. The percentage yield of but-1-ene increased relative to the cis-but-2-ene yield and the relative yield of trans-but-2-ene remained constant with increasing initial pressure of thiophene.

Table 7.7

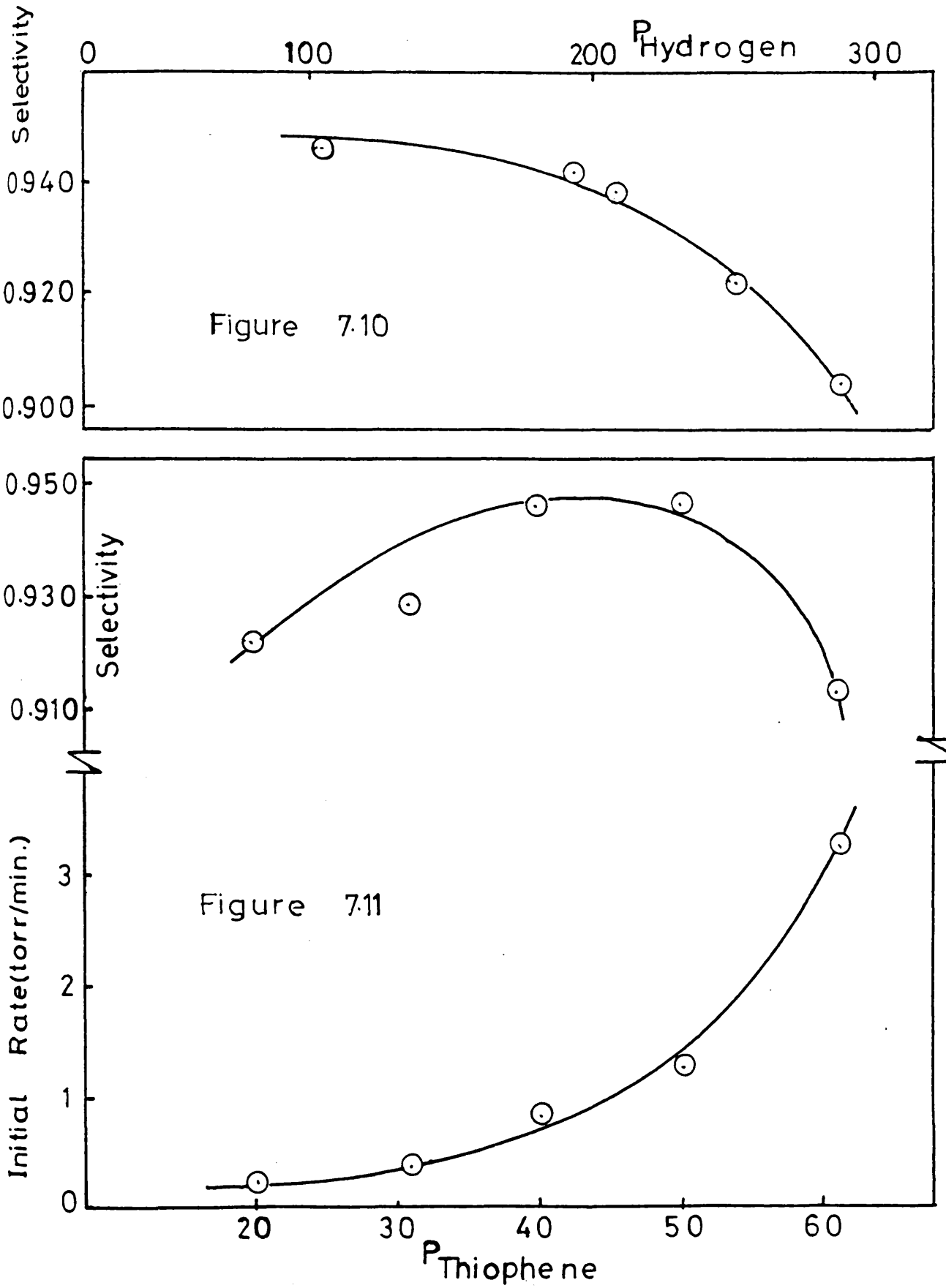
Dependence of initial rate, selectivity and total product distribution upon initial thiophene pressure

Initial hydrogen pressure = 200.0 ± 2.0 torr; temperature = 350.0 ± 2.0°C

Reaction	$P_{T.P}$ (torr)	$-\Delta P_{ext.}$ (torr)	Total product distribution (%) Pr	n-B	1-B	t-2-B	c-2-B	H_2S	(trans/cis)	1-B/2-B	Selectivity	Initial rate (torr/min)
G/5	20.0	5.0	0.0	3.7	9.4	20.9	13.0	53.0	1.61	0.277	0.921	0.25
G/4	31.0	10.0	0.0	3.3	9.8	20.4	13.0	53.5	1.57	0.293	0.929	0.67
G/3	40.0	12.0	0.0	2.5	10.0	21.1	12.5	53.9	1.69	0.298	0.946	1.00
G/1	50.0	15.0	11.8	2.4	9.3	19.1	11.0	46.4	1.74	0.309	0.943	1.00
G/2	61.0	20.0	2.5	3.6	10.6	17.8	9.5	56.0	1.87	0.388	0.913	5.00

Figure 7.10 The variation of selectivity with increasing hydrogen pressure at 350°C.

Figure 7.11 The variation of initial rate and selectivity with increasing thiophene pressure at 350°C.



7.7 The dependence of selectivity and product distribution upon temperature, and the activation energy

A series of reactions was carried out in the temperature range 294 to 402^{o}C, using a hydrogen:thiophene ratio of 4. All the reactions were analysed after a pressure fall of 20.0 $\pm$ 0.5 torr. The results show that there was no marked trend in either the selectivity or the butene distribution. The results are given in table 7.8.

From the Arrhenius plots of $\log_{10}$ (initial rate) against $^{1}/T$ (figure 7.12), a value of 44.5 $\pm$ 1.0 KJ/mole was calculated for the activation energy.

Table 7.8

The variation of selectivity, initial rate and product distribution with temperature

Initial thiophene pressure = 50.0 ± 1.0 torr; initial hydrogen pressure = 200.0 + 2.0 torr; pressure fall at extraction = 20.0 ± 0.5 torr.

Reaction	Temp. (°C)	Total product distribution (%) Pr	n-B	1-B	t-2-B	c-2-B	H_2S	(trans/cis)	1-B/2-B	Selectivity	Initial rate (torr/min.)
H/6	294	16.4	2.1	6.5	16.7	9.2	49.1	1.82	0.251	0.939	2.00
H/8	327	5.6	2.3	7.8	18.3	11.4	56.6	1.61	0.263	0.942	3.50
H/1	347	36.8	1.3	10.1	17.7	9.4	24.7	1.88	0.373	0.966	2.50
H/2	347	-	-	-	-	-	-	-	-	-	4.00
H/7	351	7.5	4.5	7.7	17.6	10.8	51.9	1.63	0.271	0.889	4.00
H/3	352	15.2	2.8	7.9	19.3	10.7	44.1	1.80	0.263	0.931	3.50
H/5	350	14.0	2.7	7.5	15.9	8.4	51.5	1.89	0.309	0.922	4.00
H/9	375	10.1	3.1	7.6	18.4	10.0	50.8	1.84	0.268	0.921	7.00
H/4	402	13.2	2.8	8.9	16.7	10.2	48.2	1.64	0.331	0.927	9.00

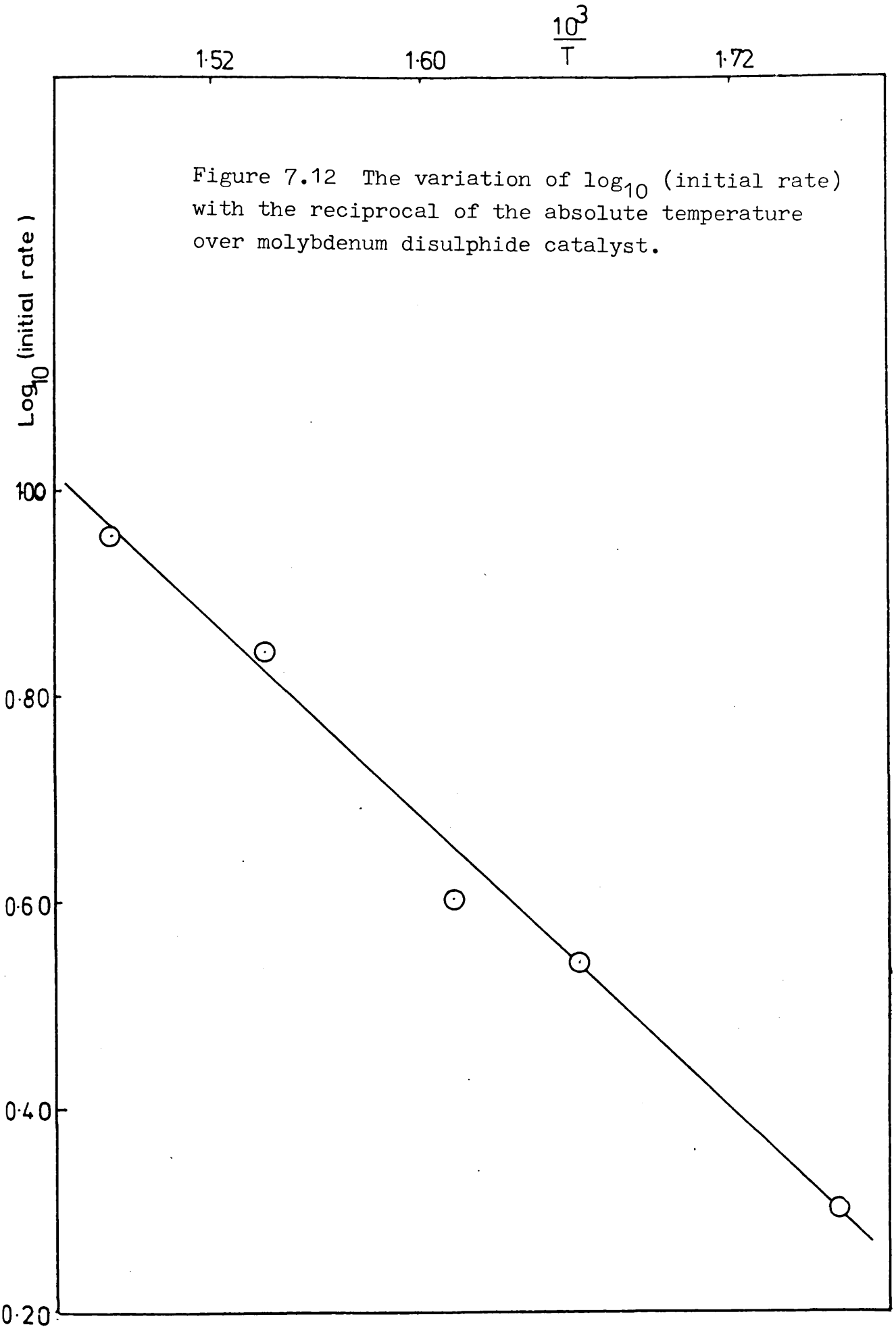


Figure 7.12 The variation of $\log_{10}$ (initial rate) with the reciprocal of the absolute temperature over molybdenum disulphide catalyst.

CHAPTER 8

8. PHYSICAL CHARACTERISATION AND THE ADSORPTION OF HYDROGEN SULPHIDE OVER MOLYBDENUM DISULPHIDE CATALYSTS

8.1 Studies of the interaction of hydrogen sulphide with molybdenum disulphide catalyst

In chapter 6 (section 6.3) the results were given of the experiments where samples of catalysts were treated with amounts of hydrogen sulphide under various conditions of pretreatments. A gradual change in the catalytic behaviour was observed as a function of hydrogen sulphide uptake. There was a limit to the change in the catalytic behaviour as a function of the total uptake of hydrogen sulphide, although the uptake of hydrogen sulphide continued after this limit had been reached. No attempt was made at that stage to determine the total amount of hydrogen sulphide required to saturate the surface of the catalyst. The experimental work described in section 6.3 revealed the desirability of investigating the interaction of hydrogen sulphide with the catalyst to determine (a) the extent of sulphur uptake by the catalyst (b) the amount of hydrogen produced as the result of sulphur uptake and (c) the extent of sulphur exchange between the gaseous hydrogen sulphide and the surface of the molybdenum disulphide catalyst. In an attempt to obtain further information about these various possibilities the experiments described below were performed.

Experiment 1

A fresh (0.3085g) sample of catalyst was heated gradually to 350°C *in vacuo* and then kept at 350°C under vacuum for about one hour. A measured amount (47.68 μm) of [^{35}S]-hydrogen sulphide was admitted to the catalyst, which was kept under [^{35}S]-hydrogen sulphide at 350°C for two hours. The gas phase material was then transferred quantitatively to the chromatograph for analysis. The results of this experiment are given below (table 8.1).

Table 8.1

Temperature = 350°C

Weight of the catalyst = 0.3085g

Amount of [^{35}S]-hydrogen sulphide taken in

= 47.68 μm

Amount of [^{35}S]-hydrogen sulphide taken up by the catalyst

= 44.48 μm (8.68×10^{19} molecules g^{-1})

Amount of hydrogen in gas phase

= 11.50 μm (2.26×10^{19} molecules g^{-1})

The ratio of [^{35}S]-hydrogen sulphide adsorbed:gas phase hydrogen

= 3.84

The [^{35}S]-hydrogen sulphide treated catalyst was then treated with nonactive hydrogen sulphide. This was carried out to examine whether the catalyst could exchange [^{35}S] with that

of the added nonactive sulphur. A known amount (13.32 μm) of nonradioactive hydrogen sulphide was introduced to the [^{35}S]-hydrogen sulphide treated catalyst, which was maintained at 350°C. The catalyst was allowed to stand under hydrogen sulphide at 350°C for 30 minutes. The analysis figures (table 8.2) show that there was an exchange between the gaseous hydrogen sulphide and the [^{35}S]labelled catalyst. The results are given in table 8.2

Table 8.2

Amount of hydrogen sulphide admitted	=	13.32 μm
Gas phase analysis: total hydrogen sulphide	=	14.90 μm
[^{35}S]-hydrogen sulphide	=	6.10 μm
nonactive hydrogen sulphide	=	8.80 μm
hydrogen (negligible)		

A large excess (~300 torr) of hydrogen was allowed to interact with the hydrogen sulphide treated catalyst at 350°C for a period of 1.5 hours. This was done to observe the possible recovery of hydrogen sulphide (active and nonactive) as the result of hydrogen treatment. The analysis figures given in table 8.3 show that very small amounts of [^{35}S]-hydrogen sulphide and nonactive hydrogen sulphide were recovered.

Table 8.3

Pressure of hydrogen admitted to the catalyst = ~300 torr

Amount of [^{35}S]-hydrogen sulphide recovered = 0.774 μm

Amount of hydrogen sulphide recovered = 0.588 μm

Experiment 2

A fresh (0.5980g) sample of catalyst was heated in vacuo to 350°C for one hour. A known quantity (39.65 μm) of [^{35}S]-hydrogen sulphide was then allowed to interact with the catalyst at 350°C for two hours. Subsequent analysis showed that the whole of the [^{35}S]-hydrogen sulphide was taken up by the catalyst. Only hydrogen was detected in the gas phase. The results are shown in table

Table 8.4

Temperature = 350°C

Weight of the catalyst = 0.5930g

Amount of [^{35}S]-hydrogen sulphide admitted

= 39.65 μm (3.99×10^{19} molecules g^{-1} catalyst)

Amount of [^{35}S]-hydrogen sulphide in gas phase

= 0.00 μm

Amount of hydrogen in gas phase

= 14.13 μm (1.42×10^{19} molecules g^{-1} catalyst)

Ratio of [^{35}S]-hydrogen sulphide adsorbed:hydrogen in gas phase = 2.81

It is evident from experiment 1 (table 8.1) that the total number of hydrogen sulphide molecules required to saturate the surface are 8.68×10^{19} molecules g^{-1} catalyst. From the results obtained in experiment 2 it was anticipated that the total number of [^{35}S]-hydrogen sulphide molecules adsorbed (3.99×10^{19} molecules g^{-1} catalyst) would not be sufficient to saturate the surface. This catalyst was therefore treated with a further quantity of nonradioactive hydrogen sulphide (45.27 μm) with a view to observe the exchange of sulphur between the surface partially covered with [^{35}S]-hydrogen sulphide and the added nonactive hydrogen sulphide. The results are shown in table 8.5.

Table 8.5

Amount of nonradioactive hydrogen sulphide admitted to the catalyst pretreated with [^{35}S]-hydrogen sulphide	= 45.27 μm
Amount of hydrogen sulphide (active and nonactive) in gas phase	= 11.47 μm
Amount of nonactive hydrogen sulphide taken up by the catalyst	= 33.80 μm
Amount of nonactive hydrogen sulphide in gas phase	= 8.37 μm
Amount of [^{35}S]-hydrogen exchanged with gas phase (45.27 μm) hydrogen sulphide	= 3.10 μm.

It is evident that, after the [^{35}S]-hydrogen sulphide treatment of the catalyst, the surface is still not saturated with hydrogen sulphide. However, although further uptake of hydrogen sulphide was observed, there was, at that stage, sulphur exchange between the surface and gas phase.

Experiment 3

A known quantity (65.78 μm) of hydrogen sulphide was allowed to interact with a fresh (0.471g) sample of catalyst at 350°C for 30 minutes. The gas phase analysis showed that there was no hydrogen sulphide in the product. The quantitative data is given in table 8.6.

Table 8.6

Temperature = 350°C

Weight of the catalyst = 0.471g

Total amount of hydrogen sulphide admitted to the catalyst = 65.78 μm

Amount of hydrogen sulphide in gas phase = 0.00 μm

Gas phase hydrogen produced by the adsorbed hydrogen sulphide = 18.75 μm

Ratio of the amount of hydrogen sulphide adsorbed: gas phase hydrogen = 3.51

These results show that the ratio between the amount of hydrogen sulphide taken up and the amount of hydrogen in the gas phase (3.51) is similar to that found in experiment 1 (3.81).

Experiment 4

In experiment 1, the amount of hydrogen produced as the result of interaction of hydrogen sulphide with the catalyst was determined. However no account of the amount of hydrogen taken up by the catalyst was made. In experiment 4 an attempt was made to determine the total amount of hydrogen taken up by the catalyst and to measure the hydrogen sulphide uptake on the hydrogen precovered catalyst. The procedure was as follows:

A fresh (0.7581g) sample of catalyst was heated *in vacuo* to 350°C, then kept at 350°C for about one hour. A known quantity (82.44 μm) of hydrogen was then admitted to the catalyst at 350°C. The catalyst was kept under hydrogen for 1.5 hour. The amount of hydrogen taken by the catalyst was measured and was found to be 40.70 μm (3.23×10^{19} molecules g^{-1} catalyst).

The hydrogen pretreated catalyst was evacuated for 30 minutes and then a measured quantity (99.29 μm) of hydrogen sulphide was admitted to the catalyst at 350°C and left for two hours. The quantity of hydrogen sulphide taken up was calculated to be 24.96 μm (1.98×10^{19} molecules g^{-1} catalyst).

From the results it can be seen that the hydrogen pretreated catalyst is capable of adsorbing a smaller amount (1.98×10^{19} molecules g^{-1} of catalyst) of hydrogen sulphide as compared to the amount (8.68×10^{19} g^{-1} of catalyst) adsorbed by the fresh catalyst (experiment 1) .

8.2 Examination by electronmicroscopy

Catalyst samples were examined using a Siemens Elumscope 1 Electron Microscope at 80kV with double condenser illumination. The morphology of different samples which had been used in the catalytic studies were examined as follows:

Electronmicroscopy of the 'fresh' sample of catalyst showed it to be in the form of large sheets which, in some cases, appeared to have folded over (plate 1).

The hydrogen sulphide treated catalyst which was used in butadiene hydrogenation reactions (see section 6.3, series A) was examined. The morphology of this catalyst shows that the material was in the form of thin sheets. A few overlapping sheets can be seen in this micrograph (plate 2).

Another sample of catalyst which had been used for butadiene hydrogenation reactions and subsequently was treated with a large excess of air (see chapter 5, page 79) was also examined. An irregular morphology was observed. Aggregation of the particles had commenced, probably as a result of the extensive treatment of the catalyst with air (plate 3).

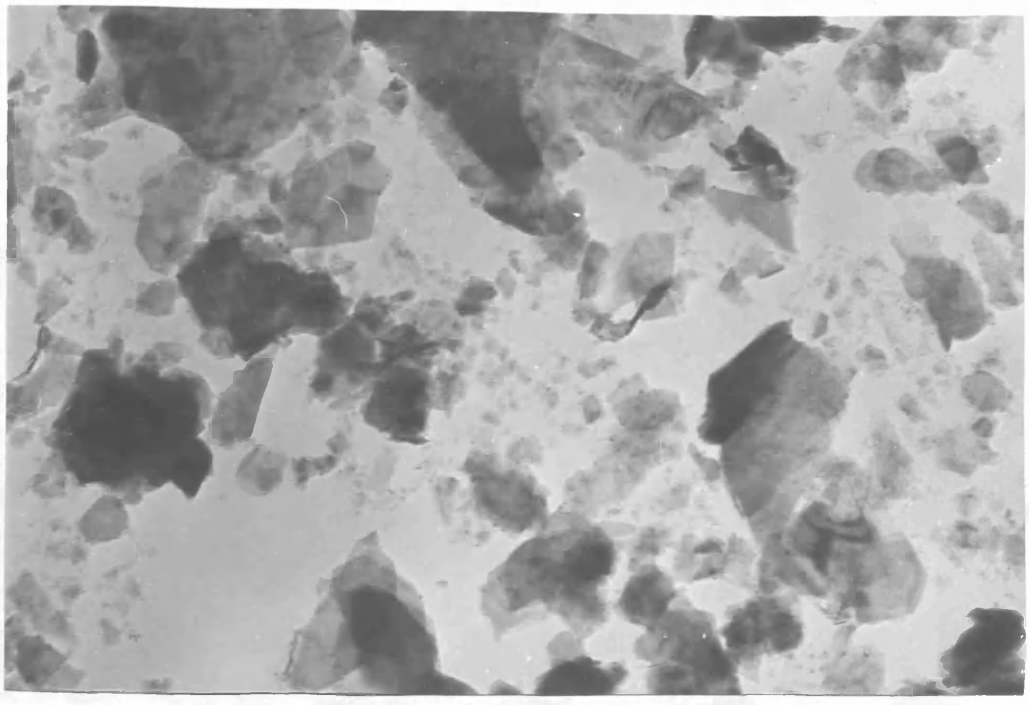


Plate I Fresh molybdenum disulphide catalyst X 60,000

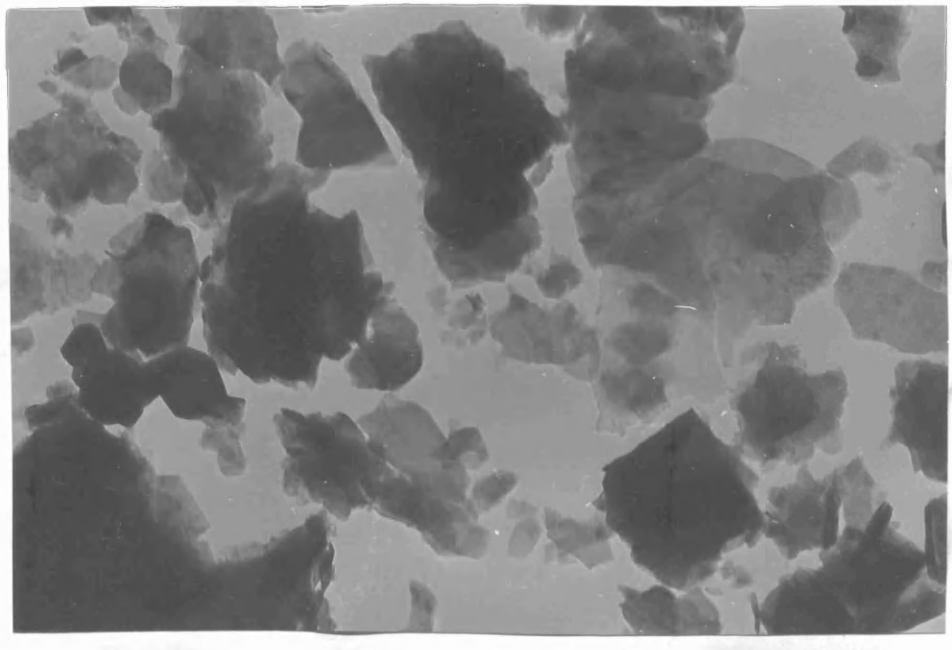


Plate 2. Hydrogen sulphide-treated molybdenum disulphide catalyst x 60,000

Plate 3. Air-treated molybdenum disulphide catalyst x 60,000

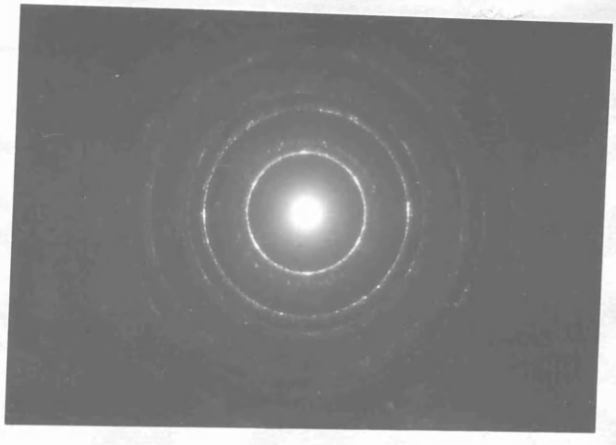


Plate 4. Electron diffraction photograph of molybdenum disulphide

Electron diffraction patterns of several samples of catalyst which had been treated under varying conditions were recorded. They were all found to show a similar diffraction pattern and all were identified as MoS_2 (molybdenite). The diffraction pattern of a fresh sample of the catalyst is shown in plate 4. Table 8.7 shows the measured 'd' spacings for a fresh sample of catalyst compared with the values of MoS_2 given in the A.S.T.M. powder diffraction file.

Table 8.7

Electron diffraction results

K = 43.36

Ring diameter (mm)	Lattice spacings dÅ	A.S.T.M. (17-744) MoS_2
16.0	2.71	2.71 (101)
16.6	2.61	2.63 (012)
others ?	-	-
27.4	1.58	1.58 (110)
28.3	1.53	1.53 (113)
others ?	-	-
32.0	1.35	1.36 (021; 202)
33.5	1.29	1.28 (205)
42.3	1.02	1.01 (214)
43.5	1.00	1.00 (125)

CHAPTER 9

9. DISCUSSION

9.1 General description of the work

Extensive use has been made of thiophene as a model compound for catalytic hydrodesulphurisation. Thiophene is one of the simplest sulphur-containing compounds and can be assumed to be representative in this class. Although hydrodesulphurisation of heterocyclic compounds has been investigated frequently to establish pathways for the reactions, our knowledge about the catalytic chemistry of these compounds is fragmentary, failing to establish structure-reactivity patterns that might shed light on the reaction mechanism. The majority of the data has been obtained on cobalt-molybdenum system with various catalyst compositions and under various reaction conditions. The other systems (nickel-molybdenum, cobalt-tungsten, nickel-tungsten) have been studied less, but it is possible to generalise, in most cases, from the results obtained on cobalt-molybdenum catalysts. Owing to differences in their components the function of all these catalysts might not be identical, but their general behaviour might be expected to be similar. In addition to this the supported system is so complicated that some simplification is needed for understanding the various phenomena which may occur. One type of simplification is to eliminate the support. Molybdenum disulphide is the most simple unsupported sulphide. Its

catalytic study is important, since relatively more physico-chemical data on textural, electrical and magnetic properties are available which could be helpful in the elucidation of mechanistic facets of thiophene hydrodesulphurisation.

Another interesting feature to emerge from the studies of thiophene hydrodesulphurisation comes from a consideration of the generally accepted mechanism for thiophene hydrodesulphurisation, as put forward by Amberg and co-workers (32). Their reaction network (figure 9.1) suggests that the first reaction of thiophene in the primary reaction path is C-S bond cleavage to form buta-1,3-diene.

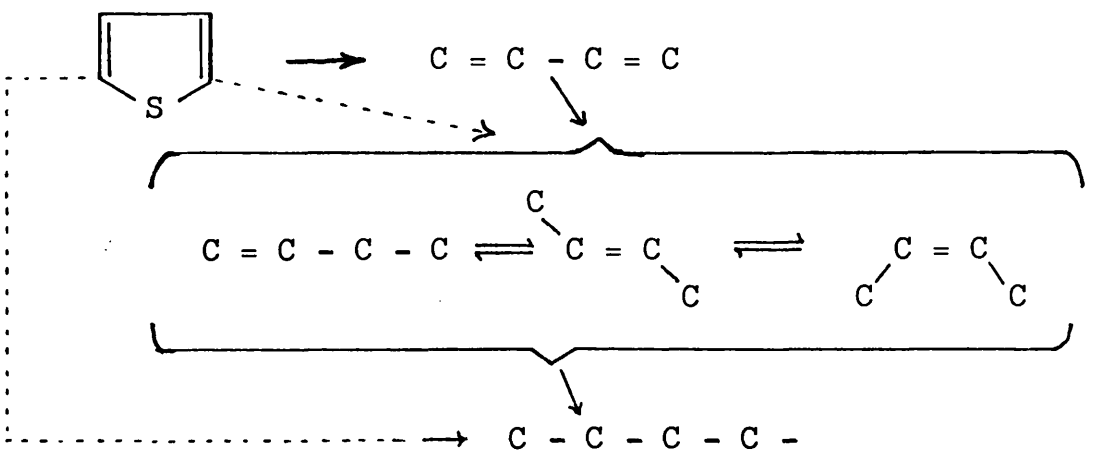


Figure 9.1 Thiophene hydrodesulphurisation

The production of buta-1,3-diene from the hydrodesulphurisation of thiophene opens a vast field of interest to use buta-1,3-diene as a probe to study its catalytic hydrogenation on an unsupported catalyst such as molybdenum disulphide.

9.2 The influence of sulphur content in molybdenum disulphide upon the hydrogenation reactions of buta-1,3-diene

In the ensuing discussion the results obtained over the fresh catalyst and over various pretreated catalysts will be presented in order to postulate possible reaction mechanisms which will explain the effect of sulphur content of the catalyst upon its behaviour. The term 'butadiene' will be used to refer exclusively to buta-1,3-diene.

The surface of molybdenum disulphide is known to be very non-stoichiometric; under sulphiding conditions the surface may contain excess sulphur, whilst under reducing conditions it may be deficient in sulphur, in the presence of oxygen or air a partial oxidation on the surface may occur (37,38,45).

Our studies in molybdenum disulphide catalysts extended the idea that catalyst pretreatments may lead to changes in the isomerisation and hydrogenation activity of the catalyst. The gas phase butadiene hydrogenation reactions were studied over these catalysts and the product distributions were examined. The influence of the following treatments was studied;

(a) hydrogen treatment;

(b) hydrogen sulphide treatment;

(c) sulphur treatment (sulphur introduced by carrying out hydrodesulphurisation reactions of thiophene);

(d) air treatment over fresh and sulphur treated catalysts;

(e) effect of sulphur removal from the catalyst;

(f) continuous pumping and evacuating the fresh and sulphur-treated catalysts.

The results reported earlier in this thesis may be summarised as follows. Two types of n-butenes distribution were obtained over these catalysts; type A, where the initial but-1-ene was the major product and the trans-cis ratio was low (ca. 1-B 58%, t-2-B 28%, c-2-B 14%) and type B, where the initial yield of but-1-ene was relatively low and the initial trans-cis ratio was high (ca. 1-B 28%, t-2-B 52%, c-2-B 20%). The results of the various treatments of the catalysts upon the butene distribution observed in butadiene hydrogenation reactions are summarised in table 9.1. The first reaction of each of the reaction series is tabulated and the corresponding behavioural type is assigned.

Table 9.1

The butene distribution after the treatment of molybdenum disulphide catalyst

Series	Description of the catalyst	Butene distribution			Type assigned
		1-B	t-2-B	c-2-B	
(1)	Fresh evacuated catalyst	30.3	43.9	28.8	B
(2)	Fresh catalyst used for series of butadiene hydrogenation reactions	58.7	27.0	14.3	A
(3)	Fresh catalyst treated with hydrogen	58.1	25.6	16.3	A
(4)	Fresh catalyst treated with hydrogen sulphide	28.3	52.7	19.0	B
(5)	Fresh catalyst treated with sulphur (sulphur introduced via hydro-desulphurisation of thiophene)	36.6	49.8	19.6	B
(6)	Sulphided catalyst where sulphur was removed by flowing N_2 at 750°C	55.5	28.6	15.9	A
(7)	Sulphided catalyst treated with air	60.1	26.8	13.1	A
(8)	The above catalyst treated with hydrogen sulphide	33.7	44.8	21.5	B
(9)	Fresh catalyst treated with hydrogen followed by air treatment	48.3	27.4	24.3	A
(10)	Fresh catalyst used for series of butadiene hydrogenation reactions followed by air treatment	46.0	39.6	14.4	A

After various pretreatments the catalysts were examined by carrying out a series of butadiene hydrogenation reactions. These reactions were performed to investigate various features of the system.

(a) The modification in the hydrogenation activity of the catalyst as the result of treatment.

(b) The variation in the hydrogenation activity with reaction number.

(c) The change in the butene distribution as the result of the treatment.

(d) The variation in the butene distribution with reaction number after the treatment.

(e) The possible removal of sulphur as the result of carrying out a series of hydrogenation reactions.

The results summarised in table 9.1 will be discussed in the light of the features mentioned above.

When a butadiene hydrogenation reaction was carried out over a fresh molybdenum disulphide catalyst which had been evacuated for about two hours before, the catalyst exhibited a typical type B behaviour. This catalyst gradually changed to a type A behaviour when further butadiene hydrogenation reactions were performed. Although no hydrogen sulphide was observed as a product, a sublimate of a brownish coloured material was observed on the cooler parts of the reaction vessel; this was presumed to be sulphur. It is therefore established that the fresh, evacuated catalyst has a type B surface which

progressively changes to type A surface when used for a series of butadiene hydrogenation reactions. The question arises as to whether this transformation of surface B to surface A can be attained by treating the fresh catalyst with hydrogen. To investigate this, the fresh catalyst was treated with hydrogen and then a series of butadiene hydrogenation reactions was performed. The results revealed that the catalyst exhibited a type A behaviour (series 3). These results may be interpreted by considering that fresh molybdenum disulphide catalyst contains a certain amount of non-stoichiometric sulphur which may be removed by evacuation, whereas relatively firmly bound non-stoichiometric sulphur is not removed by evacuation. Type B behaviour was shown by this evacuated catalyst. However, the majority of this non-stoichiometric sulphur was removed either by carrying out a series of butadiene hydrogenation reactions or by catalyst treatment with hydrogen.

The influence of the introduction of sulphur upon catalytic behaviour was investigated over a variety of catalysts. The sulphur was introduced to the fresh catalyst, either by catalyst exposure to hydrogen sulphide or by carrying out a series of thiophene hydrodesulphurisation reactions, type B behaviour was exhibited by catalysts so treated (series 4 and 5). Similarly, type B behaviour was observed when a sample of a catalyst which had been used previously for butadiene hydrogenation reactions was exposed to hydrogen sulphide. In general it may be concluded that molybdenum disulphide

catalysts which exhibited type A behaviour transform to type B behaviour when treated with hydrogen sulphide or when used for thiophene hydrodesulphurisation. The significant point to emerge is that once the type B surface has been established, it can not be reconverted to a type A surface, either by catalyst treatment with hydrogen or by performing series of butadiene hydrogenation reactions. Attempts were also made to reduce the sulphur treated surface of molybdenum disulphide catalyst to type A surface by interacting the catalyst with hydrogen for a prolonged period at elevated temperatures up to 500^{o}C. Neither hydrogen sulphide was produced nor any significant change in the butene distribution was observed with reaction number after such a hydrogen treatment. This clearly indicates that sulphur introduced to the catalyst was either firmly bound to the surface or became the part of the lattice. The possible surface-sulphur structure will be discussed in section 9.3.

The conversion of a type B surface to a type A surface could be achieved either by removing excess of sulphur from the catalyst (series 6) by heating to 750^{o}C in nitrogen or by exposing it to the atmospheric oxygen at 350^{o}C (series 7). With one sample of sulphur treated catalyst, the catalyst was placed in a furnace in a flow of nitrogen at 750^{o}C. A pale yellow sublimate presumed to be sulphur was observed on cooler parts of the vessel. This catalyst was then used for a series of butadiene hydrogenation reactions. The catalyst

exhibited a typical type A behaviour. This observation can be interpreted in two ways: first, the sulphur which was taken up by the catalyst was removed therefore type B surface was converted to type A surface. Second, it is well established fact that the solid sulphides are immediately superficially oxidised when contacted with air (50). The latter possibility can not be ignored as the sulphided catalysts were exposed to air and then transferred to an oven for removal of sulphur. However, it seems likely that both these factors affected the conversion from type B behaviour to type A. In another situation where a hydrogen sulphide treated catalyst was exposed to air, showed type A behaviour (series 7). This observation may be interpreted to mean that either a partial oxide layer was developed over the sulphide layer, or alternatively oxygen reacted with sulphur of the catalyst thus lowering its sulphur content. Sulphur dioxide although not specifically detected, was probably produced in this process. A question arises as to whether there was any possibility of converting an oxygen-treated catalyst (series 7) to a type B surface by treating the catalyst with hydrogen sulphide. The catalyst was, therefore, exposed to hydrogen sulphide and then examined for butadiene hydrogenation reactions. The catalyst exhibited type B behaviour, showing that the catalyst could be resulphided (series 8).

From reaction series 2 and 3 it is clear that the fresh catalyst attained type A behaviour, either when used by carrying out series of butadiene hydrogenation or by treating

the fresh catalyst with hydrogen. To investigate whether further modification in behaviour was possible if the catalyst was exposed to air, two samples of fresh catalysts were used separately. A fresh sample of catalyst was used for a series of butadiene hydrogenation reactions. The catalyst progressively moved towards and eventually attained type A behaviour. The catalyst was then exposed to air. The treated catalyst was then used for butadiene hydrogenation. The catalyst behaviour was not modified (series 10). In another case a fresh sample of catalyst was first treated with hydrogen then evacuated and exposed to air (series 9). After performing butadiene hydrogenation reactions over this catalyst, it was found that the catalyst showed type A behaviour. From these results it can be inferred that air had little influence on the behaviour of those catalysts, which already displayed type A behaviour. Furthermore if it is assumed that a superficial oxide layer was formed over a sulphide layer, then it could be concluded that this superficial oxide surface did not modify the catalytic function of the catalyst or, alternatively, that atmospheric oxygen did not produce the partially oxidised surface.

The introduction of sulphur to the catalyst also caused a change in the initial rate of reaction. In general the activity pattern was such that upon treatment with sulphur, the hydrogenation activity was at first enhanced. But the increased activity was not maintained; it diminished

gradually with the reaction number. The gradual decrease in the activity may be attributed possibly to the accumulation of carbonaceous materials, and polymeric species on the surface which caused a gradual blocking of the active sites. In some cases these deactivated catalysts were 'cleaned' by allowing them to stand under hydrogen for a prolonged period at an elevated temperature of around 500^{o}C. However, treatments did not successfully remove the retained species from the surface and the hydrogenation activity was not restored to its original point.

The results presented in section 6.3 show that, when various catalysts were quantitatively treated with hydrogen sulphide, a gradual response in the variation in butene distribution was observed. The results show that every small addition of hydrogen sulphide to the catalyst caused a corresponding change in the butene distribution, that is, a gradual modification from type A to type B behaviour was observed as a function of hydrogen sulphide uptake. Series of butadiene hydrogenations were carried out after each small uptake of hydrogen sulphide. There was a limit to the change in the butene distribution as a function of total hydrogen sulphide uptake, although hydrogen sulphide uptake was continued after this limit had been reached. The quantitative uptake of hydrogen sulphide which was required to achieve the maximum change in the butene distribution for various catalysts is summarised in Table 9.2.

Table 9.2

Description of the catalyst	Number of hydrogen sulphide molecules g^{-1} catalyst required to achieve maximum change in butene distribution
Catalyst, previously used for butadiene hydrogenation reactions	4.33×10^{18}
Catalyst pretreated with hydrogen	5.09×10^{18}
Catalyst pretreated with hydrogen followed by air treatment	5.33×10^{18}
Fresh evacuated catalyst	8.91×10^{18}

The introduction of hydrogen sulphide to the catalyst also caused an increase in the hydrogenation activity. However, when subsequent hydrogenation reactions of butadiene were performed, after each interaction of hydrogen sulphide, the activity diminished with use from reaction to reaction. There was an interesting similarity between the gradual change in the butene distribution and the hydrogenation activity. When at a certain stage of sulphur uptake, no modification in the butene distribution was observed, then at the same stage the hydrogenation activity also ceased to increase. The added hydrogen sulphide which caused changes in the catalytic behaviour was

not susceptible to removal either by carrying out butadiene hydrogenation reactions, or by catalyst treatment with hydrogen, or by continuous evacuation at the reaction temperature of 350°C. Furthermore, constancy in the butene distribution from one reaction to another also leads to the conclusion that added sulphur was permanently retained on the catalyst and was not susceptible to removal by performing hydrogenation reactions.

The following were the salient features of the adsorption studies of hydrogen sulphide carried out over molybdenum disulphide catalyst.

(a) Hydrogen was produced as the result of the interaction of hydrogen sulphide with molybdenum disulphide.

(b) There was practically no exchange (1.0%) between the sulphur of the fresh catalyst and gas phase hydrogen sulphide.

(c) When a catalyst fully saturated with [^{35}S]-hydrogen sulphide was treated with non-active hydrogen sulphide, there was an exchange (~60%) between the labelled surface and gas phase hydrogen sulphide.

(d) When a catalyst, partially covered with [^{35}S]-hydrogen sulphide, was treated with a further quantity of non-active hydrogen sulphide, further uptake was observed and there was, at that stage, sulphur exchanged (6.8%) between the surface and gas phase.

(e) The number of hydrogen sulphide molecules required to saturate the surface of the catalyst was 8.68×10^{19} per gram of catalyst. In contrast, the number of hydrogen sulphide molecules required to change a type A to a type B surface was $\sim 5 \times 10^{18}$ per gram of catalyst.

(f) The number of hydrogen molecules taken up by the catalyst was 3.23×10^{19} per gram of catalyst.

(g) For a hydrogen precovered surface the total hydrogen sulphide uptake was 1.98×10^{19} molecules per gram of catalyst.

In explaining these features of the adsorption of hydrogen sulphide and change of catalytic behaviour, the initial step is to consider the mode of adsorption of hydrogen sulphide on the catalyst. The production of hydrogen as the result of hydrogen sulphide uptake clearly indicates that at least some of the hydrogen sulphide was dissociatively adsorbed on surface. The reactions may be considered as occurring on the surface

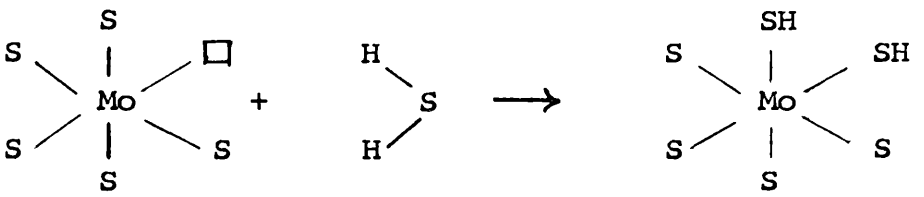
$$H_2S \longrightarrow S^{2-} + H_2(g) \qquad (1)$$

$$\square + S^{2-} + H_2S \longrightarrow SH^- + HS^- \qquad (2)$$

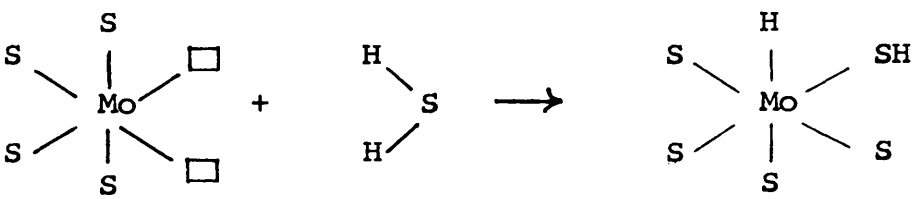
$$2\square + H_2S \longrightarrow H^+ + SH^- \qquad (3)$$

$$2\square + 2H_2S \longrightarrow 2SH^- + H_2(g) \qquad (4)$$

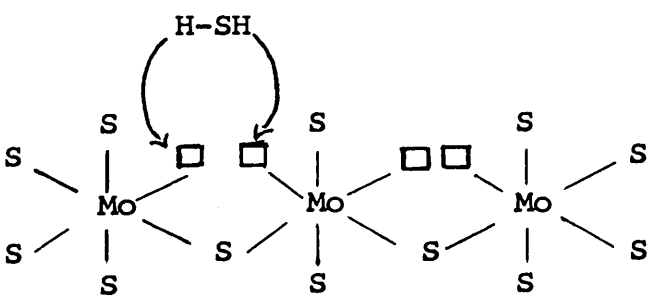
On the basis of available information about the adsorption of hydrogen sulphide and hydrogen on molybdenum disulphide, the adsorption can be illustrated as follows:



(a)

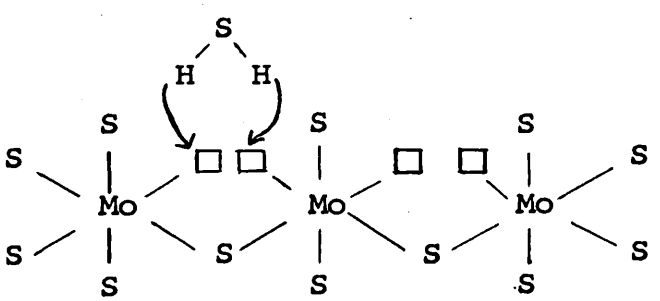


(b)

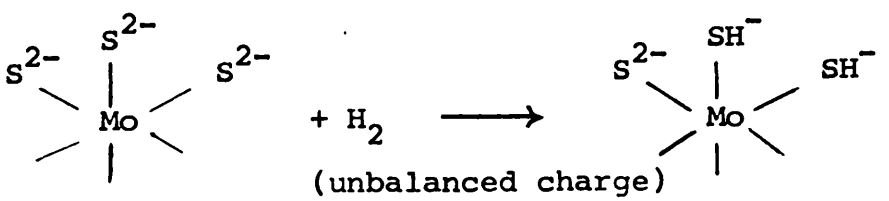


(c)

or



(d)



(e)

An important conclusion drawn from the adsorption studies of hydrogen sulphide was that, there was only a very small exchange between the sulphur of the catalyst molybdenum disulphide and the gas phase hydrogen sulphide. On the other hand, a catalyst precovered with [^{35}S]-hydrogen sulphide, when treated with non-active hydrogen sulphide gave a very significant exchange. Similarly, sulphur was exchanged between a surface partially covered with [^{35}S]-hydrogen sulphide and gas phase non-active hydrogen sulphide, even though further uptake of hydrogen sulphide was possible. It was noted above that in the catalysis of butadiene hydrogenation reactions on a type B surface, no hydrogen sulphide (active or non-active) was displaced as the result of hydrogenation reactions or by catalyst treatment with hydrogen.

In the butadiene hydrogenation reactions, it was observed that the total number of hydrogen sulphide molecules required (8.91×10^{18} g^{-1} catalyst) to cause a maximum change in the butene distribution was almost $^{1}/10$ of the total hydrogen sulphide molecules required to saturate the surface (8.68×10^{19} g^{-1} catalyst). This leads to the conclusion that a substantial amount of the hydrogen sulphide taken up by the catalyst does not take part in the actual catalysis and may become incorporated the lattice possibly producing interstitial sulphur.

There was an interesting correlation between the number of hydrogen sulphide molecules which were capable of undergoing

exchange and the total number of molecules of hydrogen sulphide molecules required to bring about the maximum change in the butene distribution and the hydrogenation activity. This exchange value (1.19×10^{19} molecules g^{-1} catalyst) was in the same range as the value (8.91×10^{18} molecules g^{-1} catalyst) which brought maximum change in the butene distribution. It may therefore be concluded that the adsorbed sulphur which causes the change in the surface from type A to type B behaviour is also exchangeable with gas phase hydrogen sulphide. The remaining sulphur does not participate in the modification of the catalytically active surface.

These conclusions are in agreement with earlier observations by Kalechits and co-workers (43,45). They found that non-stoichiometric sulphur enters into the surface layers of the lattice where it can be removed easily during benzene hydrogenation (43). According to these workers, sulphur in the fresh catalyst can be divided into three parts.

(i) Most of the sulphur (90 - 95%) is firmly-bound stoichiometric sulphur, which cannot be removed by hydrogenation and cannot be exchanged.

(ii) The remaining sulphur is removable. Most of this labile sulphur can be removed by hydrogenation, although a part can only be exchanged with gas phase hydrogen sulphide. Both types of labile sulphur were involved in the catalytic behaviour of the molybdenum disulphide for benzene hydrogenation reactions.

Hydrogen was produced as the result of the interaction of hydrogen sulphide with molybdenum disulphide. It was therefore found in a separate experiment that the total number of molecules of hydrogen taken up by molybdenum disulphide catalyst was 3.23×10^{19} per gram of catalyst. This significant amount of hydrogen taken up by the catalyst could be attributed to the sorption of hydrogen, since sorption of hydrogen over molybdenum disulphide catalyst is a well known phenomenon (14). The spacing between layers, 2.96 Å, seems to be sufficient for hydrogen molecules to penetrate the solid (94). The hydrogen-precovered catalyst was capable of adsorbing a smaller amount of hydrogen sulphide (1.98×10^{19} molecules g^{-1} catalyst) as compared with the amount adsorbed by the fresh catalyst (8.68×10^{19} molecules g^{-1} catalyst). This was probably due to preadsorbed hydrogen hindering dissociation of hydrogen sulphide molecules on the surface, with the result that there was a smaller hydrogen sulphide uptake. Unfortunately no measurements of the amounts of hydrogen displaced as the result of the interaction of hydrogen sulphide with the hydrogen precovered surface of molybdenum disulphide could be made during the present study.

9.3 Mechanism of buta-1:3-diene hydrogenation

The main results of the researches discussed in the foregoing sections of this thesis may be summarised by considering the variations in catalytic behaviour, as measured by changes in the distributions of the n-butenes formed in buta-1:3-diene hydrogenation, of the molybdenum disulphide catalysts arising from various catalyst treatments. These are shown schematically in figure 9.2, where the butene distribution is plotted as a function of the number of hydrogenation reactions performed over the catalyst.

Examination of this figure shows that there is a direct correlation between the amount and exchangeability of 'sulphur' on the catalyst surface and the ability of the latter to promote either type 'A' behaviour, with but-1-ene as the major product, or type 'B' behaviour, with trans-but-2-ene as the major hydrogenation product. Thus, a freshly prepared catalyst sample, which is capable of some sulphur exchange with [^{35}S]-hydrogen sulphide, progressively becomes a type 'A' surface with catalyst usage and, in the process loses a small amount of sulphur. This type 'A' surface, once established, behaves reproducibly with respect to buta-1:3-diene hydrogenation and does not undergo sulphur exchange with [^{35}S]-hydrogen sulphide. However, extensive treatment of the type 'A' surface with either hydrogen sulphide or with a series of thiophen-hydrogen mixtures results in a ready conversion to a type 'B' surface, on which sulphur exchange occurs

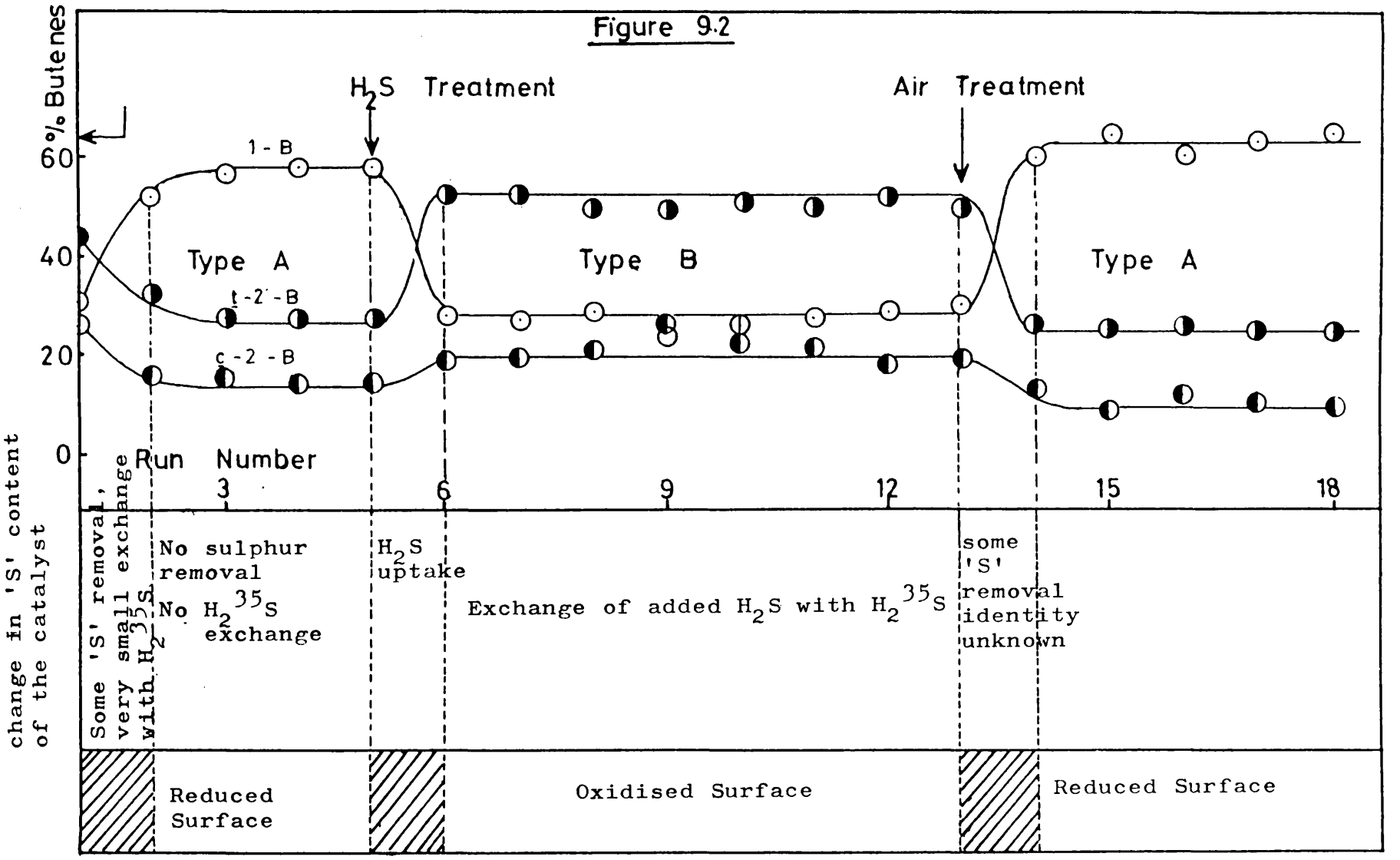


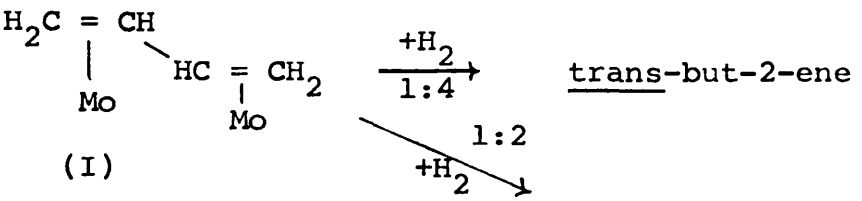
Figure 9.2
% Butenes
60
40
20
0
H_2S Treatment
Air Treatment
1 - B
t - 2 - B
c - 2 - B
Type A
Type B
Type A
Run Number
3
6
9
12
15
18
change in 'S' content of the catalyst
Some 'S' removal, very small exchange with $H_2{}^{35}S$
No sulphur removal
No $H_2{}^{35}S$ exchange
H_2S uptake
Exchange of added H_2S with $H_2{}^{35}S$
some 'S' removal identity unknown
Reduced Surface
Oxidised Surface
Reduced Surface

between the "added" sulphur and gas phase hydrogen sulphide. Once formed, the type 'B' surface, like the type 'A' surface, is stable and behaves reproducibly with regard to the hydrogenation of butadiene.

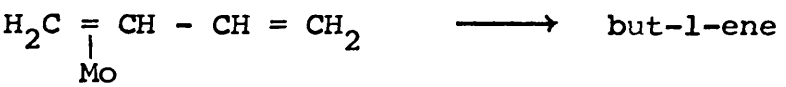
From the hydrogen sulphide adsorption results discussed in Section 9.2, it is apparent that most of the hydrogen sulphide uptake corresponds to the formation of surface SH^- ions, rather than S^{2-} surface species. If, as suggested by Tanaka and Okuhara (94), the active surface sites are co-ordinatively unsaturated molybdenum ions, then it is possible to envisage that one of the major differences between the types 'A' and 'B' surface lies in the oxidation state of the surface molybdenum ions and that the distribution of butenes, formed by butadiene hydrogenation on each type of surface, is a reflection of the differing states of oxidation of the molybdenum ions on the two surfaces. Thus whilst both the type 'A' and 'B' surfaces contain coordinatively unsaturated molybdenum ions and may, therefore, be considered to be reduced relative to stoichiometric molybdenum disulphide, the type 'B' surface will be oxidised relative to the type 'A' surface, although the precise nature of the molybdenum ions on either surface cannot be deduced from the present work.

Over both the type 'A' and type 'B' surfaces the variations of the butene distributions with hydrogen uptake are consistent with a mechanism whereby both the but-1-ene and but-2-ene are formed directly from butadiene by, respectively,

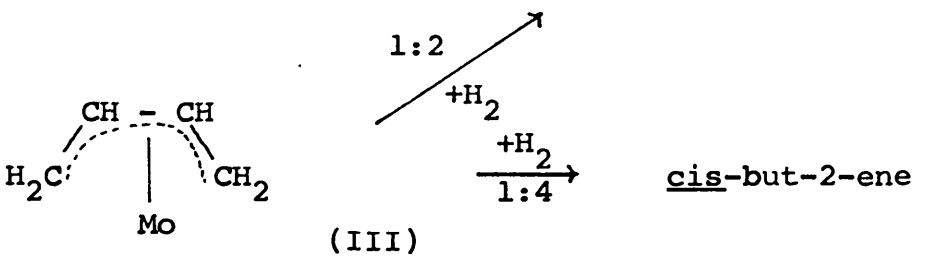
1:2- and 1:4-addition of hydrogen, rather than by 1:2-addition of hydrogen followed by double bond migration of but-1-ene to form cis- and trans-but-2-ene. The following mechanisms may be considered

(a) 

(I)

(b) 

(II)

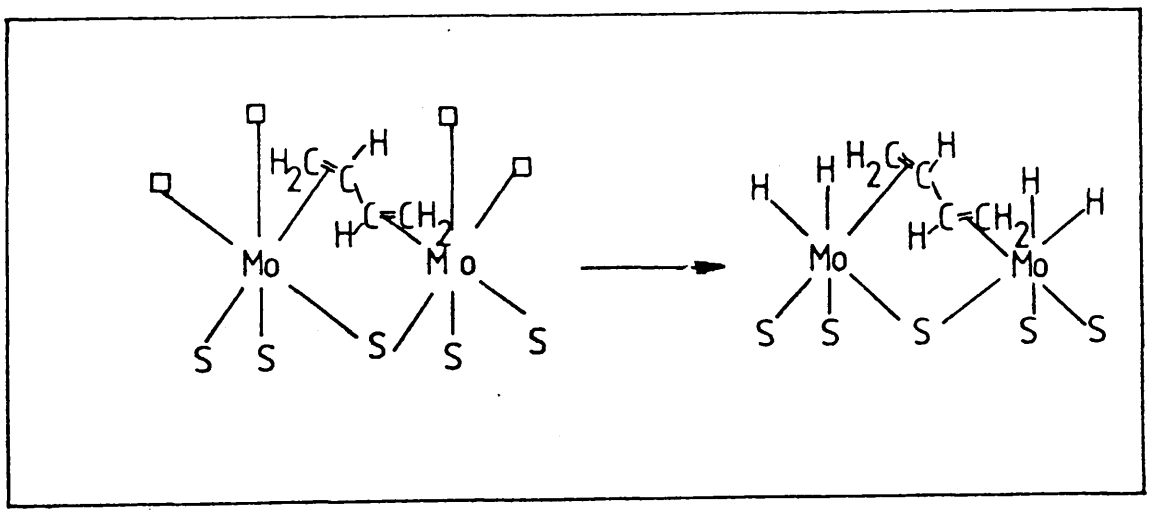
(c) 

(III)

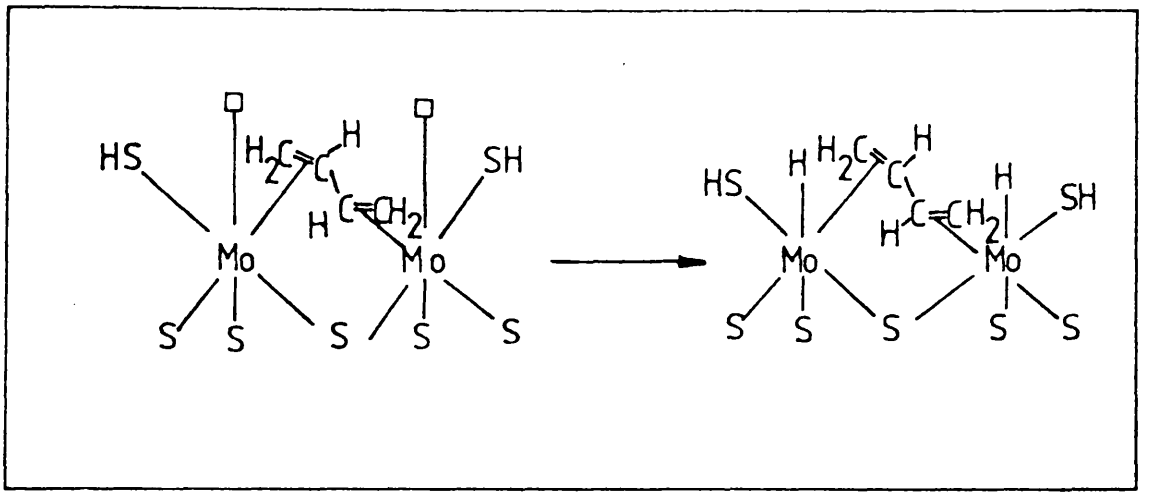
The relatively high yields of but-1-ene and trans-but-2-ene, as compared to the yield of cis-but-2-ene, suggests that, on both type 'A' and 'B' surfaces, species (I) and (II) are more likely than species (III), possibly due to steric restrictions associated with the formation of (III).

The relative amounts of species (I) and (II) is unclear at this stage. Whilst it has been established that but-1-ene isomerisation occurs on the molybdenum disulphide catalysts suggesting that adsorbed species similar to species II are

possible, it is also possible that species (I) may be solely responsible for the but-1-ene and trans-but-2-ene yields. In this case the differences in behaviour of the type 'A' and 'B' surfaces could be ascribed to a difference in the availability of hydrogen for 1:2- and 1:4-addition, depending upon the degree of coordinative unsaturation of each molybdenum ion,



type 'A' surface (1:2-addition favoured)



type 'B' surface (1:4-addition preferred)

such that, at the type 'A' surface each molybdenum ion could be considered as being bonded to the hydrocarbon and two hydrogen atoms enabling 1:2-addition to occur. Conversely, at the type 'B' surface each molybdenum ion is envisaged as bonding to the hydrocarbon and one hydrogen atom, which, on steric grounds favours 1:4-addition to the adsorbed butadiene. A more extensive study of the availability and mode of activation of molecular hydrogen would be required to substantiate unequivocally between these various possibilities.

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